

ADVANCES IN CHEMICAL PHYSICS
VOLUME VIII

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ADVANCES IN CHEMICAL PHYSICS—VOLUME VIII

I. Prigogine—Editor

The Application of Wave Mechanical Methods to the Study of Molecular Properties

Edited by R. DAUDEL

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PREFACE

The present book contains some of the main papers presented at the International Summer Institute held at Menton, France (July 1-14, 1963). This institute was organized under the auspices of NATO and the patronage of Professor Louis de Broglie, Nobel Prize. The book is divided into two parts. The first is concerned with the electronic structure and the spectra of molecules and crystals. The second part is devoted to chemical and biochemical problems.

R. D.

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PART I

**ELECTRONIC STRUCTURE
AND SPECTRA**

SOME RECENT DEVELOPMENTS IN THE QUANTUM THEORY OF MANY-ELECTRON SYSTEMS AND THE CORRELATION PROBLEM

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The main problem in the quantum theory of the stationary states of many-electron systems is the solution of the Schrödinger equation $H\Psi = E\Psi$. It is often convenient to write the Hamiltonian in the form $H = H_0 + V$, where V is considered as a perturbation which is not necessarily small. Following the original idea of Schrödinger, we will introduce a *single* unperturbed eigenfunction φ_0 , satisfying the relations

$$H_0\varphi_0 = E\varphi_0, \quad \langle\varphi_0|\varphi_0\rangle = 1 \quad (1)$$

From this starting function, the exact solution is derived by means of a *wave operator* W , such that

$$\Psi = W\varphi_0, \quad \langle\Psi|\varphi_0\rangle = 1 \quad (2)$$

Combining these two relations, one obtains for the energy,

$$E = \langle\varphi_0|H\Psi\rangle = \langle\varphi_0|H_0 + V|\Psi\rangle = E_0 + \langle\varphi_0|VW|\varphi_0\rangle.$$

In this connection it is hence convenient to introduce the reaction operator t by the relation $t = VW$, which gives the energy shift

$$E = E_0 + \langle\varphi_0|t|\varphi_0\rangle, \quad t = VW \quad (3)$$

Formal expressions for the wave and reaction operators are easily derived by means of the partitioning technique,¹ which leads to the formulas

$$t = V + V \frac{P}{(E_0 - H_0) - (V - \langle\varphi_0|t|\varphi_0\rangle)} V \quad (4)$$

$$W = 1 + \frac{P}{(E_0 - H_0) - (V - \langle\varphi_0|t|\varphi_0\rangle)} V \quad (5)$$

Here $P = 1 - |\varphi_0\rangle\langle\varphi_0|$ is the projection operator for the part of the Hilbert space which is the orthogonal complement to φ_0 .

By using the infinite series

$$(A - B)^{-1} = A^{-1} + A^{-1}BA^{-1} + A^{-1}BA^{-1}BA^{-1} + \dots,$$

one can easily derive the basic formulas in Brillouin's and Schrödinger's perturbation theories. We note that the formulas (4) and (5) are equivalent to the results of infinite-order perturbation theory.

Most of the present development in the study of many-particle systems is devoted to efforts to find convenient forms for the wave and reaction operators. The importance of the reaction operator has been stressed particularly by Brueckner and his group. If the total Hamiltonian has symmetry properties, it is often feasible to let W contain the standard group-algebra projection operators associated with the symmetry group. The alternant molecular orbital method and the general method using "different orbitals for different spins" are both based on this idea. In other cases (Bohm and Pines and others), the wave operator has been approximated by a numerical factor expressing the correlation between the motions of the particles and particularly the collective oscillations. In connection with the self-consistent-field schemes, one has had a development based on the analogy between the energy expectation value $\langle\varphi_0|H_0 + V|\varphi_0\rangle$, which forms the basis for the variation principle in the standard Hartree-Fock scheme, and the exact energy value $\langle\varphi_0|H_0 + \dagger|\varphi_0\rangle$. A comparison shows that one can improve the formalism of the independent-particle model by replacing the perturbation V by the reaction \dagger . For further details and complete references, we will refer the reader to some other papers.²

References

1. Löwdin, P. O., *J. Chem. Phys.* **19**, 1396 (1951); *Advan. Chem. Phys.* **2**, p. 207, particularly p. 270 (1959); *J. Math. Phys.* **3**, 969 (1962); *J. Mol. Spectr.* **10**, 12 (1963).
2. Löwdin, P. O., *J. Mol. Spectr.* **10**, 12 (1963); *J. Math. Phys.* **3**, 969 (1962); *ibid.* **3**, 1171 (1962); *Rev. Mod. Phys.* **35**, 702 (1963).

CALCULATION OF TRANSITION ENERGIES FROM THE GEOMETRY OF THE SYSTEM

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In its most simple form, the calculation of transition energies for molecules with conjugated ethylenic bonds can be carried out by the method normally called LCAO MO. This type of calculation requires the introduction of a dynamic parameter, usually written γ , which represents the exchange integral calculated over two neighbouring atomic orbitals $2p_z$. The value of γ is usually taken from experiment. It allows us to reproduce systematically the resonance energies of the various molecules and, less satisfactorily, the transition energies as measured spectroscopically. Another method, usually known as the free-electron method, allows the calculation of the transition energies without necessitating the introduction of the dynamic parameter and taking into account only the geometry of the molecule.

The two methods have a definite relation which comes from the fact that the structure of the molecule, and particularly its dimensions, is regulated by the value of the exchange energy. We thought it possible to specify this relation by using the essential peculiarity of the free-electron model, that is, the elimination of all dynamic constants by the LCAO MO method.

We will, first of all, briefly resume the method^{1, 2, 3} of calculation by considering the particularly simple case of the electronic transitions of the π electrons of ethylene. The problem may be treated, to a first approximation at least, as a mono-electronic problem. The normal orbital N is, as is well known, described by the $2p_z$ orbitals of the bound atoms, written ψ_1 and ψ_2 , and the overlap integral S by:

$$\Phi_1 = (\psi_1 + \psi_2)/\sqrt{2(1 + S)}$$

The method consists of considering all the wave functions Φ_2, Φ_3, \dots representing the excited levels and of representing

the function $x\Phi_1$, where x is the coordinate taken from the axis defined by the bound atoms, by means of the expansion

$$x\Phi_1 = x_{11}\Phi_1 + x_{21}\Phi_2 + x_{31}\Phi_3 + \dots$$

The element x_{11} is zero if the origin is taken at the centre of symmetry of the molecules. We assume, therefore, that one of the transitions is preponderant, for example, $\Phi_1 \rightarrow \Phi_2$. We may then represent the function Φ_2 by:

$$x_{21}\Phi_2 = x\Phi_1 \quad (1)$$

In this relation, x_{21} is defined by the normalization condition:

$$x_{21}^2 = \int x^2 \Phi_1^2 d\tau$$

which we write thus because Φ_1 is real.

The interest of Eq. (1) is that it permits the calculation of the transition energies. We have:

$$E_2 = \int \Phi_2 H \Phi_2 d\tau = \frac{1}{x_{21}^2} \int x \Phi_1 H (x \Phi_1) d\tau$$

The integral may be evaluated without having to write the expression for the Hamiltonian because we have:

$$Hx = xH - \frac{h^2}{4\pi^2m} \frac{\partial}{\partial x}$$

We obtain:

$$E_2 = E_1 + \frac{h^2}{8\pi^2m x_{21}^2}$$

The transition energy $E_2 - E_1$ may be obtained from the structure of the molecule without the explicit use of any dynamic parameter. It is only necessary to write x_{21}^2 , that is:

$$x_{21}^2 = \frac{1}{(1+S)} \int x^2 (\psi_1^2 + \psi_1 \psi_2) d\tau -$$

If r represents the length of the bond C—C, we obtain immediately

$$\int x^2 \psi_1^2 dr = \frac{r^2}{4} + \xi^2$$

where

$$\xi^2 = \int x_1^2 \psi_1^2 d\tau$$

the origin being chosen at the centre of atom 1. We also write

$$\eta^2 = \int x^2 \psi_1 \psi_2 d\tau$$

In the following calculations, we neglect the value of η . For ξ , we obtain, using Slater-type orbitals,

$$\xi^2 = 24a_0^2/Z^{*2}$$

where a_0 is the radius of the first Bohr orbit and Z^* is the effective atomic number. We obtain:

$$\rho^2 = 4(\xi^2 + \eta^2); \quad x_{21}^2 = \frac{r^2 + \rho^2}{4(1 + S)}$$

$$E_2 - E_1 = \frac{h^2(1 + S)}{2\pi^2 m(r^2 + \rho^2)}$$

These relations are of exactly the same form as those obtained using the free-electron model taking into account the quantity which is usually called the "end" correction, and which appears here as an arbitrary factor. The value for the wavelength of the transition thus calculated is $\lambda = 1575 \text{ \AA}$, against 1630 \AA , the usual experimental value. This agreement is very satisfactory considering that the integral η is taken as zero. Taking into account the value of this integral increases the calculated value of λ .

From this agreement, we presume that the wave function $x\Phi_1$ must represent the wave function of the excited state in a satisfactory manner. In the LCAO representation, the latter is given by:

$$\Phi_2 = \frac{\psi_1 - \psi_2}{\sqrt{2(1 - S)}}$$

We should therefore obtain:

$$x \frac{\psi_1 + \psi_2}{\sqrt{2(1 + S)}} = x_{21} \frac{\psi_1 - \psi_2}{\sqrt{2(1 - S)}}$$

Thus, forming the scalar product with Φ_2 :

$$x_{21} = \frac{\gamma}{2\sqrt{1-S^2}}$$

Comparing this with the value obtained above, we have:

$$S = \frac{\rho^2}{\gamma^2 + \rho^2}$$

With the above approximation ($\eta = 0$), we obtain $S = 0.22$. It is obvious that this value is lowered in such a way that the agreement is very satisfactory.

Finally, let us study the results obtained and compare them with those obtained by the LCAO method. In this method, the energies of the two levels, π and π^* , are respectively:

$$E_1 = Q + \frac{\gamma}{1+S}; \quad E_2 = Q - \frac{\gamma}{1-S}$$

from which we obtain the bond energy of the π electrons, $E_\pi = 2|\gamma|/(1+S)$, which can be compared to that of the transition energy, $2|\gamma|/(1-S^2)$. Using the expression which we have just calculated for the transition energy we obtain:

$$E_\pi = \frac{h^2}{2\pi^2 m \rho^3} S(1-S^2)$$

The quantitative agreement is not good. This arises in part from the fact that ρ has been underestimated and in part also from the fact that a great number of approximations have been used. It is nonetheless true that the approximate proportionality of E_π and S correspond to the generally accepted result:

$$\gamma/S \approx \text{constant}$$

We have tried to apply this method to several cases, notably those of *trans*-butadiene^{4,5} and benzene,⁵ using antisymmetrized Slater orbitals to form the initial wave function. The function in Φ_2 , the excited state, is then supposed to be of the following form:

$$K\Phi_2 = \left(\sum_{r=1}^4 x_r\right)\Phi_1 = X\Phi_1$$

where the summation is over the coordinates of the four π electrons. The calculation offers no particular difficulty, but introduces an arbitrary factor, the direction of the Ox axis. The orientation which corresponds to an energy extreme for the excited level is approximately that of a median C—C bond for the *trans*-isomer. The corresponding wavelength of 2089 Å is very close to the experimentally measured value of 2100 Å.

The case of benzene is treated in the same way starting from an antisymmetrized orbital formed on an LCAO MO basis. The value obtained for the transition energy, 2687 Å, is slightly greater than the experimental value, 2550 Å. It is possible that the value chosen for the parameter S , namely 0.218, is slightly low.

The advantage of this method is that it allows the calculation of transition energies from the geometry of the molecule. It is evidently based on a postulate: the existence of a transition from the ground state to a single excited state. It is difficult to say to what degree this postulate is valid. We have, therefore, endeavoured to find more elaborate wave functions but have always tried to avoid the use of dynamic parameters. It is for this reason that in the case of ethylene,⁶ we have used the following form for the excited orbital:

$$C\Phi_2 = [(x_1 + x_2) + \alpha(x_1^3 + x_2^3) + \beta(x_1^2x_2 + x_2^2x_1)]\Phi_1$$

α and β being determined by the variational method, which preserves the u -type symmetry of Φ_2 . The calculations are longer but without any particular difficulty. They were carried out using a Craig-type orbital for the ground state:

$$N\Phi_1 = A_1A_2 + pB_1B_2$$

where

$$A = \frac{a + b}{\sqrt{2(1 + S)}}, \quad B = \frac{a - b}{\sqrt{2(1 - S)}}$$

For

$$\begin{array}{ll} p = 0, & N - V = 1894 \text{ Å} \\ p = -0.0777, & N - V = 1627 \text{ Å} \\ p = -0.3572 \text{ (Craig's value),} & N - V = 900 \text{ Å} \end{array}$$

This result has led us to propose for the ionic contribution a value very much smaller than that suggested by Craig. In any case, one reservation must be made, the method supposes essentially that we are interested in a parallel transition, that is, one without variation in the separation of the nuclei.

The same method has been adapted to the study of the triplet transition by looking for an excited-state orbital which is antisymmetric in the space coordinates, and is therefore of the form :

$$N\Phi_3 = Y(1 + \lambda Y^2 + \mu X^2)\Phi_1$$

where

$$X = x_1 + x_2, \quad Y = x_1 - x_2$$

The coefficients λ and μ are again determined by the variational method, which gives the transition 2194 Å. This seems to be in reasonable accord with the experimental value.

This method may also be applied to the calculation of polarizabilities. Indeed, we arrived at the present formulation of this method when wishing to perform such calculations. More recently,⁷ it has been applied to the problem of calculating the polarizability of ions having the rare gas structure. Here again the ground state is considered as being described by an antisymmetric function composed of Slater orbitals. The excited orbital was taken to be of the form :

$$N\Phi = (1 + \lambda X)\Phi_1$$

with

$$X = \sum_{r=1}^n x_r$$

where n represents the number of valence electrons. The value of λ is obtained by the variational method by calculating the energy

$$E = \int \Phi^*(H_0 - efX)\Phi d\tau$$

More elaborate wave functions have been set up by using an expansion similar to that above but using more terms. Examination of the different possibilities shows that it is best to take a function of the type :

$$\Phi = \Phi_1(A_0 + A_1 \sum_i x_i + A_2 \sum_i x_i^3 + A_3 \sum_i x_i^5)$$

with a small contribution from the term x_i^5 . As an example, we will give the values of the polarizability found for ions having the neon structure:

Factors:

$$\begin{aligned} A_0 + A_1 \Sigma x_i & \quad \alpha_1 = \frac{9800}{9} a_0^3 / Z^{*4} \\ A_0 + A_1 \Sigma x_i + A_2 \Sigma x_i^3 & \quad \alpha_2 = \frac{10,225.22}{9} a_0^3 / Z^{*4} \\ A_0 + A_1 \Sigma x_i + A_2 \Sigma x_i^3 + A_3 \Sigma x_i^5 & \quad \alpha_3 = \frac{10,236.19}{9} a_0^3 / Z^{*4} \end{aligned}$$

The results thus obtained have allowed us to set up a table of polarizability increments by a method somewhat different from that of Pauling. The starting point is the polarizability of the isoelectronic rare gas, in our case neon, which has been measured experimentally and which allows us to calculate a value of Z^* (4.55 in these calculations). The values $Z^* \pm 1$ used respectively for the ions Na^+ and F^- permit us to obtain respectively $0.177 \times 10^{-24} \text{ cm}^3$ for Na^+ and $1.06 \times 10^{-24} \text{ cm}^3$ for F^- . The apparent atomic numbers are much lower than those obtained using Slater's rules (5.85 for Na^+). This is to be expected from the fact that, following Slater's rules, these numbers determine the energy of the shells and thus the electronic behaviour reasonably close to the nucleus, while in the present work they were deduced from values of the polarizability where the electronic atmosphere comparatively far from the nucleus plays a predominate part. A final application of the method⁸ is the study of the confined ions such as exist within the crystalline lattice of the halides. We have endeavoured to treat this case in a similar way to that of the free ion, simulating the confinement by means of a Fermi function. If, therefore, Φ_0 represents the wave function of the free ion, we write:

$$\Phi = \Phi_0 f(r_0, \lambda)$$

where r_0 represents the cut-off and λ the steepness. The procedure is to fix r_0 and to determine λ by variation in order to find an energy extremum. The comparatively simple calculation for the case of a single electron, which is without much interest, becomes

much more complicated in the case of the simplest ion, Li^+ . This is because of the modifications necessary to the apparent atomic number due to the effect of compression. These calculations can only be carried out by means of an electronic computer. The principal point of interest in this calculation is that it enables direct calculation of the compression energy of the ion. The origin of this energy is the electronic confinement, a consequence of the Pauli principle. The calculation gave a repulsion which may be reasonably expressed by Born's term in B/r^n with $n = 7.77$, which appears to be an acceptable order of magnitude.

The compression energies so calculated are higher than the experimental values unless r is relatively large. It is scarcely possible to consider values of the ionic radius of Li^+ less than 0.9 Å. This is in agreement with the experimentally determined plot of electronic densities but is very much above the values normally accepted (Goldschmidt, 0.78 Å, and Pauling, 0.60 Å).

It must be mentioned that such values were obtained from the apparent atomic numbers which we have already criticized.

In conclusion, let us say that even though the method becomes rather complicated here because the factor in polynomial form is replaced by a Fermi function, we consider that the method nevertheless presents a certain interest because at the same time it gives a solid base for comparison between the LCAO model and the metallic model.

References

1. Barriol, J., and Regnier, J., *Compt. Rend.* **237**, 307 (1953).
2. Barriol, J., and Regnier, J., *J. Phys.* **15**, 528 (1954).
3. Barriol, J., and Regnier, J., *J. Phys.* **16**, 641 (1955).
4. Barriol, J., and Regnier, S., *J. Chim. Phys.* **53**, 929 (1956).
5. Barriol, J., and Regnier, S., *J. Chim. Phys.* **54**, 231 (1957).
6. Barriol, J., and Regnier, J., *Colloq. Intern. Centre Natl. Rech. Sci. (Paris)* 205 (1958).
7. Weislinger, E., *J. Chim. Phys.* **55**, 528 (1958).
8. Weislinger, E., D.Sc. Thesis, University of Nancy, 1963.

OPTICAL ABSORPTIONS AND CHARGE TRANSFER STATES

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The physical processes that we shall analyze are the optical absorptions in salts and crystals of paramagnetic ions. It is essential to have a proper understanding of the mechanism which causes the absorption or emission of light in these materials. The quantitative measure of our understanding is (in principle) the success or otherwise of the intensity calculation; that is, we take the experimental values of the intensities or, better, of the oscillator strength of the bands or lines and see whether they agree with the values that a theoretical calculation, based on some mechanism, gives.

Apart from the intrinsic merit of understanding what goes on, there is also the non-negligible advantage in the understanding of the mechanism that it provides a check on the assignment (that is, the identification of an observed line with an energy level). Actually, there have been some cases in the past where a mistaken assignment could have been avoided by making a calculation of the expected intensity.

After this preface about the role and uses of intensity calculation I turn now to give some of the details of my past calculations of the intensities of the crystal-field spectra, but mainly I intend to dwell on the reasons which underlie these calculations.

First of all we need a *model* for the calculations, since I feel very strongly that if only we can find a suitable framework for the calculations, that is, one which gives the essentials of the situation, the way for the calculation is already mapped out (perhaps not unambiguously as regards details, but certainly as regards the direction in which to proceed). I shall therefore spend some time on the background of the problem before describing the actual calculation.

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Although the absorptions (or emissions) all take place in either the liquid or the solid phase, i.e., when the metal ion and its immediate neighbors are embedded in either a dielectric or in a crystal, we shall neglect almost completely the embedding field and look for the energy levels of the electrons in the molecular complex made up of the metal and its immediate neighbors. (This molecule is frequently, when there are six ligands, a regular octahedron or, for four ligands, a regular tetrahedron.) I might add that the embedding field, which will be the Madelung potential in ionic solids and a polarization field in dielectrics, can be approximately regarded as a potential uniform throughout the volume of the complex. In many cases this amounts to a raising of all electronic levels.

Going over now to the calculation of electronic levels in the complex, we can subdivide the range of energy levels into three regions. I might call these three divisions the region of deep-lying occupied states, the intermediate region and the region of high, excited states. I shall now describe these regions.

In region one of the deep-lying occupied levels nothing can go wrong: these levels and the corresponding wave functions (w.f.) are without any doubt identical, or practically so, with those of the states of either the central ion or the ligands taken separately. (There will be a uniform shift in all levels, though, as I have already mentioned.) This uninteresting region houses all inner-shell electrons, and one reason why practically nothing changes in this region as the result of the electrons being in a molecular complex is that the electronic radii are below the radius of contact between ligands and the ion.

The second region is characterized by just the inverse condition, namely that the electronic radii are approximately equal to the contact radii. This region accommodates the outer shell, which for most ligands is a closed shell. As regards the ion, if this is a transition-metal ion, the region certainly includes the d -electrons of the partly filled shells ($3d$, $4d$, or $5d$, as the case may be), and it may also include some neighboring shells. The criterion ought really to be, as I shall soon try to show, the size of the electronic orbit. In this region the electrons of the complex retain much of the character that they had in the free ion or ligand (this is due to some extent to the closed-shell structure of most of the ligands

and also to the high symmetry of the ligand arrangement). This is true at least to the extent that transitions in the complex could all be assigned in terms of states of the free ions, as much as atomic transitions could be assigned in terms of one-electron jumps between l or j states. (This situation in the molecular complexes is in contrast with that in, say, homonuclear molecules.) The main novelty in the complex is that because of overlap of the central and peripheral electronic wave functions there will be covalency effects. This means that one adds to the ligand w.f. a metal component, and vice versa. It is doubtful at present whether this superposition is a sufficiently good approximation or whether perhaps a certain amount of expansion of the radial part of the wave function, or perhaps even some other modification of the w.f. (compatible only with its symmetry), is needed. At present, then, there is no certainty on this point.

When we go higher in the scale of electronic energies, we reach the third region. We are tempted to carry on with the scheme which filled in the lower two regions and place in the third region the states of the empty, excited, ionic electrons, modified by covalency effects (but not too much: still retaining the character of the original ionic state). We can, however, see quite clearly that this procedure is wrong for the actual molecular arrangement. The point is that, as I have already remarked before, the size of the molecular complex is related to the size of the outermost filled or partly filled shell, whereas the size of the excited orbitals is much in excess of this and just cannot be fitted into the space available for the metal ion. In somewhat more accurate language this effect would be expressed in terms of the exchange energy between the excited ionic w.f. and the w.f. of the ligands, and I should like to assert that I believe that, in most of the cases, the magnitude of the exchange energy is high enough to raise the electronic energy above the ionization limit, that is, into the continuum. To be able to prove this in a particular case I should have to work out the exchange or repulsion energy; at the very least, I should have to have a knowledge of the radius of the excited state. The latter should actually be available (say, from the data of the intensities of transitions in the gaseous state). Unfortunately, I do not have this information. However, I have made a guess. This guess, which may be wrong but probably not

by much, has been arrived at by an extension of the schemes for calculating the screening constants in atoms. I find for the case, which is perhaps the most important to us, that, when the partly filled shell is the $3d$ shell and the excited state is the ionic $4p$ state, the values for the electronic radii are about 0.5 and 1.5 Å. There is now a very simple way to estimate the repulsion energy in the $4p$ state. Our understanding of ionic molecules tells us that if the electron were forced to stay in its excited $4p$ state, then the equilibrium position of the ligands would be one Ångström farther out. (This would not be a stable equilibrium position, because the ligands would get too far away from each other, but this instability would be primarily a lateral one and does not affect our argument very much.) If we now calculate the elastic energy that it costs us to bring the ligands from their new equilibrium position one Ångström inwards to their actual position, we find that we have to add to the electronic energy an amount $\frac{1}{2}k(\delta R)^2$, where k is the force constant for the displacement (which is of course a measure of the exchange energy primarily) and δR is the inward displacement. For the kind of breathing-type vibration that we encounter in the complexes, δR , which is 1 Å in our case, is about thirty times Q , the amplitude of the zero-point motion, so that

$$\frac{1}{2}k(\delta R)^2 = \frac{1}{2}kQ^2(\delta R/Q)^2 = \frac{1}{2}\hbar\omega(30)^2 = 180 \times 900 = 162,000 \text{ cm}^{-1}.$$

This, plus the purely electronic energy ($\sim 100,000 \text{ cm}^{-1}$), is indeed above the ionization limit (which is on the average $\sim 250,000 \text{ cm}^{-1}$).

It is only right to point out the shortcomings of this simple calculation, which first of all uses the same force constant for the excited-state configuration as for the ground state and thereby probably overestimates the energy. However, we also expect strong anharmonicities to come into play and, if they do, then we shall have underestimated the energy. In any case, the strongest argument against the existence of these excited states in the complex is that they have not been observed at all, and whereas this does not yet prove that they do not exist, this, together with the foregoing argument, places the burden of the proof for their existence on us, before we make such an assumption.

Unfortunately, the existence of these bound states has

frequently been taken for granted, and not only for the calculation of intensities but also in calculations of the quadratic Stark effect or in the equivalent calculations of the effect of asymmetric crystal fields. These calculations are consequently suspect, and it is a healthy sign of the state of affairs that in most instances these calculations have indeed led to numerical disagreements.

In addition to these excited ionic orbitals there are also those orbitals which arise from the excited states of the ligands. The size of these orbitals is also considerably greater than the contact radius, so that, on the face of it, the same considerations of instability ought to be applied here, too. However, there is the difference that the *ligand* excited states can expand outwards, without extending inwards in the direction of the metal ion. This may sound a bit forced, but there is really nothing artificial in it: it is simply the result of the formation of an antibonding molecular orbital, which is known to have a nodal plane between the ligands and the metal ion.

Finally, region 3 will include those w.f.'s that we get when one or more electrons are promoted from the occupied states of region 2 to the unoccupied states of that region or when electrons get promoted from the deeper region 1 to region 2. Because of the sheer number of the ligands, and because frequently most of the ligand orbitals in region 2 of the energy range are occupied, we get in this class 3 a preponderance of those excited many-electron w.f.'s in which an electron is transferred from an occupied ligand orbital (of region 2) to an unoccupied state (also of region 2) on the central ion. In such an excitation a charge transfer has taken place whose direction is clearly $L \rightarrow M$ (ligand to metal).

We shall now discuss briefly the nature of these charge transfer states (c.t.s.), since they will enter quite decisively into the intensity calculations. I shall also include in the discussion that other class of c.t.s. to which I referred earlier, namely, that which involves an excited ligand orbital and which is related to the ground state of the complex by the circumstance that an electron which in the ground-state was on the central ion got transferred to the excited ligand state, thus giving us an excited configuration. In opposition to the previous case, the direction of the transfer is now $M \rightarrow L$.

There are thus these two kinds of excited charge transfer states

in which there is a transfer between the metal and the ligand. A very important feature of these c.t.s.'s is that *they exist*, that is to say that they have been observed. They fall in the range from $35,000\text{ cm}^{-1}$ to as far into the ultraviolet as only the techniques of observation permit experimentalists to see. In many of the metal oxides only the beginnings of the band are seen. On the other hand, there are cases (such as the higher-transition-metal complexes) where the whole band, or several bands, coming from charge transfer transitions have been seen. What one sees are big broad bands. To give some values: the widths could be of the extent of $6000\text{--}8000\text{ cm}^{-1}$, and the area under the absorption curve, which is the measure of the absorption intensity, is about 1000 (or more) times larger than the area of the crystal-field absorption bands. The reason for the different intensities is of course well known. It is that in complexes in which there is a symmetry of inversion Laporte's rule holds and the strong transition will be to those c.t.s.'s which are antisymmetric with respect to the center.

On the other hand, crystal-field transitions take place between a pair of orbitals and so they are forbidden. Why they occur at all, although with diminished intensity, is just what I want to discuss after I have finished with the charge transfer states.

So, for one thing, we can observe these c.t.s.'s. Admittedly only the antisymmetric types are observed, for the reason just given. Still, there is no doubt that the symmetric-type states must also be hidden there in about the same energy region. The question, whether the transition is $L \rightarrow M$ or $M \rightarrow L$, has no *a priori* answer; rather, each case must be examined from the point of view of circumstantial evidence.

The reason that I am elaborating in such detail on these c.t.s.'s is that they are practically the only states in region 3, and also I believe that if we can only get a clear understanding of these states, the question of optical transition will sort itself out automatically. There are also many other effects in molecular complexes where the c.t.s.'s enter. I have already mentioned the cases of the quadratic Stark effect and of the asymmetric crystal field, where the c.t.s.'s must be allowed to play an equally important and indeed analogous role. A further effect relates to the width of the charge transfer bands. The main cause of the breadth is essentially the same as that for the width of the crystal-field spectrum, except that it is much

more pronounced for the charge transfer absorptions. This cause is the Frank-Condon effect, and in physical terms it means that in different electronic states the equilibrium position changes and therefore our description of the ionic motion in one electronic state does not hold for another state. In the terminology of the usual description of ionic motion in crystals, that is, in terms of phonons, this means that the phonons, instead of being infinitely long lived, have (because of the inter-mixture of different phonon pictures corresponding to different electronic states) a finite life-time. Some calculations on phonon life-time in ionic crystals have been made, but these referred to anharmonic effects which are quite distinct from the effect being discussed here.

Coming to our subject proper, to the intensities of the crystal-field bands, we take our stand on the long established guess or recognition that these are electric dipole transitions assisted by vibrations of the complex. The evidence for this is mainly that as the temperature is varied the magnitude of the intensity follows the famous cotangent law:

$$\text{Intensity} \propto \coth \hbar\omega/kT$$

with a frequency ω which is characteristic of the vibration of the complex. There may be some other cases in which the transition is a magnetic-dipole or electric-quadrupole transition: the experimental distinction for these cases is trivially simple, since with these mechanisms there is no temperature variation in the strength of the absorption. The same is true for complexes where the metal ion is subject to an antisymmetric electric field, such as when it is surrounded by four ligands arranged at the corners of a tetrahedron. The theory that I am going to give applies also, with slight changes, to such static "distortion" from the symmetric situation, so there is no restriction in principle here. I should like to add, however, that it is a pity that the question of how much of the absorption in these tetrahedral complexes is due to the static environment and how much to thermal motions has so far not been resolved experimentally by measuring the intensity over a wide enough temperature range.

Let me try now to give a brief and simple mathematical description for the transition probability, confining myself to octahedral complexes. This is essentially a quantum-mechanical perturbation

calculation, where the basic non-perturbational part is that which we have tacitly used in building up the energy-level scheme. The perturbational part will be that which adds to the potential for the electron an antisymmetric component. This is denoted by

$$H_v = H_o + H_t$$

and it splits up into two parts, which correspond to the odd field caused first by the motion of the two polar ligands (this is to all intents and purposes the vibration of a linear triatomic molecule along its axes) and secondly, by the motion of the four transverse ligands with respect to the metal ion. (This resembles an out-of-plane motion of a five-atomic planar molecule.)

We shall now work out explicitly the results of our previous level-scheme calculation, at least as far as those states which enter the discussion are concerned. I shall take the triply ionized state of chromium, Cr^{3+} , as an example. This has three $3d$ -electrons in its partly filled shell. The d -electrons split up in the environment of a positively charged regular octahedron into three t_{2g} (denoted by t) and two e_g (e) states, the former being the more stable. The energy scheme is

$\text{Cr}^{3+}: t^2\beta$	odd	C	$M \rightarrow L$	Region 3
$t^3e\alpha^{-1}$	odd	C'	$L \rightarrow M$	

$Bt^2e - Ate^2$ $At^2e + Bte^2$	even	T_1		Region 2
t^2e	even	T_1		
t^3	even	A_2		
Subshell configuration		type		

We note that there are two T_1 -type states—both are made up of states of the same two subshell configurations, but, of course, in different proportions. (These are given by the numbers A, B .) This effect comes about through the inter-electronic interaction. We have placed into region 3 those two types ($L \rightarrow M$ and $M \rightarrow L$)

of c.t.s. which we introduced earlier. (α , β denote the ligand states, and the exponent -1 over α refers to a *hole* state.) I make the point that these two types virtually exhaust the region 3 states.

It is clear that the observed optical transition in which $A_2 \rightarrow T_2$ is really the one-electron jump $t \rightarrow e$, $A_2 \rightarrow T_1$ is also the jump $t \rightarrow e$. The double-electron jump $t^2 \rightarrow e^2$ is not observable and this component of T_1 does not contribute to the intensity. Further, the observed charge transfer transition $A_2 \rightarrow C$ is the one-electron jump $t \rightarrow \beta$, and similarly $A_2 \rightarrow C$ is really $\alpha \rightarrow e$.

We now write down by perturbation theory the state functions (denoted by $|\rangle'$) which take H_v into account in terms of the eigenstates, $|\rangle$, of the original Hamiltonian.

$$|A_2\rangle' = |A_2\rangle + |C\rangle \frac{\langle C|H_v|A\rangle}{E_A - E_C} + |C'\rangle \frac{\langle C'|H_v|A\rangle}{E_A - E_{C'}} \\ |T_2\rangle' = |T_2\rangle + |C\rangle \frac{\langle C|H_v|T\rangle}{E_T - E_C} + |C'\rangle \frac{\langle C'|H_v|T\rangle}{E_T - E_{C'}}$$

The electric dipole operator P will now connect $|A_2\rangle'$ and $|T_2\rangle'$ in the form of four characteristic terms

$$\frac{\langle A|P|C\rangle\langle C|H_v|T\rangle}{E_T - E_C} + \frac{\langle A|P|C'\rangle\langle C'|H_v|T\rangle}{E_T - E_{C'}} \\ + \frac{\langle T|P|C\rangle\langle C|H_v|A\rangle}{E_A - E_C} + \frac{\langle T|P|C'\rangle\langle C'|H_v|A\rangle}{E_A - E_{C'}}$$

In terms of one-electron matrix elements this transition dipole is written as the following four types of terms:

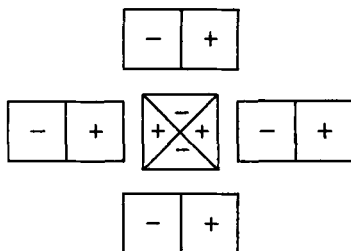
$$\frac{\langle t|P|\beta\rangle\langle\beta|H_v|e\rangle}{E_T - E_C} + \frac{\langle e|P|\alpha\rangle\langle\alpha|H_v|t\rangle}{E_T - E_{C'}} \\ + \frac{\langle e|P|\beta\rangle\langle\beta|H_v|t\rangle}{E_A - E_C} + \frac{\langle t|P|\alpha\rangle\langle\alpha|H_v|e\rangle}{E_A - E_{C'}}$$

Only types of terms appear here so that a summation over the many different α 's and β 's (the charge and hole transfer states) is understood; also H_v contains many (nine) terms; and, further, the letters t and e may denote different components of the species. In spite of the complicated form, I have been able to eliminate

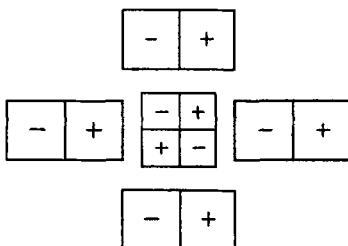
by *symmetry* arguments a good many terms and then use *physical* arguments to pinpoint the most important ones in the remainder. To be specific, in my first paper on the subject I regarded the polar motion as much more important for the transition probability than the transverse, out-of-plane vibration.

Agreement with experiment was easy and good (with the minimum amount of fiddling with parameters) for the spin-conserving transitions in the iron-series metal complexes. At present, I have no strong reason to retract from the physical arguments given in that work, except on one point. The reason which made me reconsider my conclusion is the increasing amount of recent evidence, both experimental and theoretical, for π -bonding.

Consider the central cross-section of the complex, first for an e -type electron with the signs of the w.f. and therefore also the symmetry properties indicated. In addition to the (even) e -type w.f., I have also drawn the (odd) c.t. w.f. which is going to be coupled to the e w.f. when the odd H_v is included.



Consider now the t -electron



At the time of writing my paper I was under the impression that (in the iron series, at least) the σ -bonding or overlap between

the σ -electron and the c.t. w.f. in the polar positions was overwhelmingly more important than π -bonding between t orbitals and the transverse part of the c.t.s. So I selected as the dominant mechanism a horizontal ionic motion (to ensure maximum σ -bonding) and an electric dipole in the vertical direction. Now I tend to favor rather a vertical motion giving an effective π -bonding and a horizontal dipole.

The important difference in these alterations is that in the earlier conception the first and fourth terms dominated the dipole moment matrix, while, according to the present way of thinking, the second and third terms are important. Now, I had no way of knowing whether C (i.e. $M \rightarrow L$) or C' ($L \rightarrow M$) was the important c.t.s., because experimental evidence for the iron series was very dubious and contradictory. I had found, however, that the experimental intensity data show an unambiguous dependence which goes as the inverse square of the difference between the c.t. energy and the energy of the final state (T_2 in our case) and not the energy of the initial (A_2) state. So, since I had to choose between the first and the fourth terms, I decided on the first, which showed that C was involved, or a $M \rightarrow L$ process. Now that the choice appears to be between the second and the third terms, it is the second term which has the required energy denominator. This involves now a C' or an $L \rightarrow M$ process.

I might add that the $(E_{\text{c.t.}} - E_{\text{final}})^{-2}$ law seems to be a modest universal law of nature, i.e., one holding under circumstances where one could see no strong *a priori* reasons for excluding the terms in the matrix elements which have $(E_{\text{c.t.}} - E_{\text{initial}})$ in the denominator. In fact, I have been able to fit the intensity data of the $4d$ and $5d$ hexafluorides quite well to the law: intensity $\propto (E_f - E_i) \times (E_{\text{c.t.}} - E_f)^{-2}$. (Here the first factor arises from the statistics of the photons which are being absorbed.) I have managed to justify this law as opposed to the one with $(E_{\text{c.t.}} - E_i)^{-2}$, and also managed to work out the numerical details of the mechanics, but I do not think that I have done these anything like as convincingly as either the iron series or the universality of the law seems to warrant.

It is essential, I believe, to bear in mind this last point, which is essentially the *inherent* flexibility of the calculations of intensities, or indeed of any non-diagonal matrix element. I have found

repeatedly that it is very easy to get a factor *two* either through a mistaken choice of parameters or through a tendentious "correction". There are only a few cases which are immune from human uncertainties, and I want to present now such a case.

We have already noted that for Cr^{3+} (or V^{2+} or Ni^{2+} , also) there are two T_1 states and that the transition from the ground state to these is made possible through a one-electron jump to the same component, t^2e . The ratio between the probabilities for the occupation of this component in the upper and lower T_1 state is simply A^2/B^2 (in the notation we have used). The ratio of the intensities of the bands will be proportional to this ratio, which (I should say) can be calculated from the energy matrix quite reliably. Other quantities which will enter the ratio of the two intensities will be various energy differences; there will, however, be no overlap integrals or other "subjective" quantities in the ratio of intensities. I have recently used the expression for the intensity ratios (for Ni^{2+} to be precise) to obtain values for the energies of the charge transfer band. In most cases the obtained values fall into the region where they are expected to be; for the rest, I venture to suggest that more accurate determination of the intensities will give reliable values for $E_{\text{c.t.}}$. Since that work I have seen further data (for V^{2+} , Cr^{3+} , and Ni^{2+}) which also confirm that the intermediate states are necessarily charge transfer states.

References

Extensive references to earlier experimental and theoretical works are contained in:

- Ballhausen, C. J., *Introduction to Ligand Field Theory*, McGraw-Hill, New York, 1962.
Griffiths, J. S., *The Theory of Transition Metal Ions*, University Press, Cambridge, 1961.
Jørgensen, C. K., *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, London, 1961.
McClure, D. S., *Solid State Phys.* **9**, 399 (1959).

The point of view of the present article is outlined in:

- Englman, R., *J. Chem. Phys.* **32**, 299 (1960); **38**, 1452 (1963).
Englman, R., *Mol. Phys.* **3**, 48 (1960); **4**, 183 (1961), **6**, 345 (1963).

Some papers related to the subject of the article that have appeared since the end of 1962:

- Ferguson, J., *J. Chem. Phys.* **39**, 116 (1963).
 Ferguson, J., Wood, D. L., and Knox, K., *J. Chem. Phys.* **39**, 881 (1963).
 Grum-Grzhimailo, S. V., Brilliantov, N. A., Sviridov, D. T., and Sviridova, O. N., *Opt. Spectry, USSR (English Transl.)* **14**, 118 (1963).
 Knox, K., Shulman, R. G., and Sugano, S., *Phys. Rev.* **130**, 512 (1963).
 Koide, S., and Mizuno, Y., *Helv. Phys. Acta* **36**, 530 (1963).
 Kuwabara, G., *Bull. Am. Phys. Soc.* **8**, 24 (1963).
 Lohr, L. L., Jr., and Lipscomb, W. N., *J. Chem. Phys.* **39**, 1007 (1963).
 Low, W., and Rosengarten, D. D., *J. Mol. Spectr.* **12**, 319 (1964).
 McClure, D. S., *J. Chem. Phys.* **38**, 2289 (1963).
 McClure, D. S., *J. Chem. Phys.* **39**, 2850 (1963).
 McFarlane, R. M., *J. Chem. Phys.* **39**, 3118 (1963).
 Mookherji, A., and Chhonkar, N. S., *Indian J. Phys.* **37**, 375 (1963).
 Moorjani, K., and McAvoy, N., *Phys. Rev.* **132**, 504 (1963).
 Morosin, B., and Lawson, K., *J. Mol. Spectr.* **12**, 98 (1964).
 Naiman, C. S., and Linz, Arthur, *Proceedings of the Symposium on Optical Masers*, Polytechnic Press, Brooklyn, 1963, p. 369.
 Nashimiya, S., *J. Phys. Soc. Japan* **18**, 1719 (1963).
 Poole, C. P., and Itzel, John F., Jr., *J. Chem. Phys.* **39**, 3445 (1963).
 Pysh, E. S., Jortner, J., and Rice, S. A., *J. Chem. Phys.* **40**, 2018 (1964).
 Sturge, M. D., *Phys. Rev.* **130**, 639 (1963).
 Sugano, S., and Shulman, R. G., *Phys. Rev.* **130**, 517 (1963).
 Tsujikawa, I., *J. Phys. Soc. Japan* **18**, 1391 (1963).
 Weakliem, H. A., and McClure, D. S., *J. Appl. Phys. Suppl.* **33**, 347 (1962).
 Weakliem, H. A., *J. Chem. Phys.* **36**, 2117 (1962).
 Wood, D. L., Ferguson, J., Knox, K., and Dillon, J. F., Jr., *J. Chem. Phys.* **39**, 890 (1963).

MODEL CALCULATIONS IN THE THEORY OF MIXED-CRYSTAL SPECTRA

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I. Introduction

The absorption spectra of pure molecular crystals are of value in the study of the energy levels of free molecules, and in exemplifying the Davydov splitting and inter-state mixing that occur under the influence of intermolecular forces.¹ A closer understanding of these effects will bring out new detail about the intermolecular forces themselves, of the way in which they lead to the preferred molecular packing in crystals, and of crystal dynamics. By far the most information pertaining to crystal properties has been extracted in the past from work on pure, or nearly pure, crystals, but spectroscopic studies of deliberately introduced impurity ("guest") molecules in "host" crystals have also helped to elucidate the nature of free-molecule transitions,

as in McClure's work on naphthalene as guest in durene.² There the host crystal is treated simply as a matrix to hold the guest in a known orientation, its interactions with the guest being supposed insufficiently strong to falsify conclusions based on the oriented gas approximation. Host-guest interactions have been examined in mixed crystals of tetracene in anthracene, and in some other examples, and rather clear evidence of their reality obtained,^{3,4} but again the information is about the guest molecule rather than about the host crystal.

The purpose of this paper is to examine by calculations of simple models the spectroscopic behaviour expected of mixed crystals under varying conditions of guest concentration and of guest optical properties. We shall begin by reviewing some points of the theory of pure crystals, then go on to introduce the one-dimensional model, apply it to a series of representative examples, and finally consider its relevance to real mixed crystals.

II. Pure Crystals

In molecular crystals the forces between molecules are much smaller than those within molecules. It is for this reason adequate in dealing with the low electronically excited states to use the free-molecule wave functions and to treat crystal perturbations on them only in a higher approximation. Accordingly we shall denote by $\varphi, \varphi^1, \varphi^2, \dots, \varphi^r, \dots$, the several electronic states of the free molecules, and show by subscripts (i, j) the location of the chosen molecule in the crystal. In a crystal of N molecules with h in each unit cell, the complete set of molecules is contained in the product wave function

$$\Phi_G = \varphi_{11}\varphi_{12} \cdot \cdot \cdot \varphi_{21}\varphi_{22} \cdot \cdot \cdot \varphi_{h, N/h} \quad (1)$$

in which the first subscript gives the unit-cell site and the second designates the unit cell in which the molecule is placed. Inter-molecular electron exchange being neglected, Eq. (1) is the wave function for the crystal ground state.

When one molecule is raised to its excited state φ^r the localized excitation function, Eq. (2), is one of an N -fold degenerate set, because the excitation site can be any one of the N molecules.

$$\phi_{i_p}^r = \varphi_{11}\varphi_{12}\varphi_{13} \cdot \cdot \cdot \varphi_{i_p}^r \cdot \cdot \cdot \varphi_{h, N/h} \quad (2)$$

To make excited state functions with correct symmetry it is necessary to take linear combinations of the localized excitation functions, and these must transform as do the representations of the space group of the crystal. We arrive in this way at delocalized excitation wave functions, Eq. (3),

$$\Phi_i(\mathbf{k}) = \sqrt{h/N} \sum_p \exp(i\mathbf{k} \cdot \mathbf{r}_{ip}) \quad (3)$$

the summation being over all molecules occupying sites of type i . The crystal wave functions are ordered by the values of \mathbf{k} , the wave vector, of which the modulus is inversely proportional to the wavelength of the excitation wave. There are similar expressions for the other sites, giving in all as many distinct functions $\Phi_i(\mathbf{k})$ as there are molecules in the crystal. Crystal eigenfunctions are found by combining functions belonging to a given \mathbf{k} , and to different unit-cell sites.

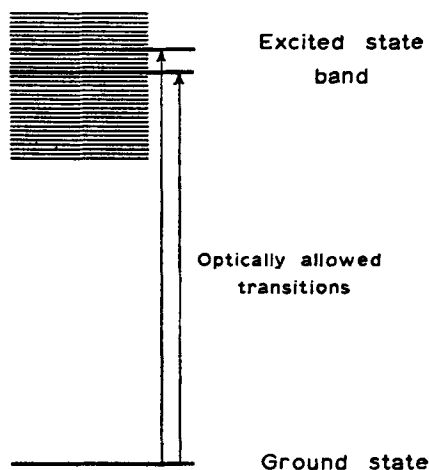


Fig. 1. Schematic diagram of the band structure of a two-molecule-per-cell crystal.

It may be shown that there are optically allowed transitions from the ground state (1) to excited states formed by combining expressions (3) only for $\mathbf{k} = 0$. There are just a small number of spectral lines in each band of \mathbf{k} values. The number of allowed transitions is equal to or less than the number of molecules in the

unit cell, and the situation is that most of the levels in an excitation band are spectrally inactive. The observed transitions show the positions of some or all of the $\mathbf{k} = 0$ levels, but never the full extent of the band structure. Figure 1 shows schematically some of the levels in the exciton band of a crystal with two molecules in the unit cell.*

III. Mixed Crystals

Mixed crystals are formed by replacement of some host molecules by others similar in dimensions and in their interactions with neighbours. Impurity or "guest" molecules with lower transition energies can capture or trap excitation energy from the "host" crystal.

An important quantity is the *trap depth* δ , which for present purposes is the difference between the lowest transition energies of a free host molecule and a free guest molecule. Among shallow traps (trap depth small compared with the intermolecular coupling energy) there is the important example of naphthalene as guest in a host crystal of octa-deuteronaphthalene. Isotopic substitution alone distinguishes host and guest; intermolecular interactions are almost identical and only the excitation energies are different. The trap depth in this example is about 100 cm^{-1} , and other similar isotopically distinguished host-guest pairs may be chosen with trap depths of as little as 10 cm^{-1} . The equivalent temperature δ/k is about 140°K when $\delta = 100\text{ cm}^{-1}$, and in what follows it will be taken that the temperature of the crystals is much lower than this and that thermal effects may be neglected. Among deep traps tetracene molecules in an anthracene host crystal provide an example. The free-molecule excitation energies of host and guest and their intermolecular interactions differ; in a first approximation the difference in interactions is ignored because mixed crystals appear to form only when the host-guest interactions are not too different from those of host and host. This statement is rather vague, but cannot be made more precise at the present time.

If the free-molecule transition energies to states $\varphi^1 \dots \varphi^r$ of the host are $\Delta w^1 \dots \Delta w^r$, the transition energy to the lowest level

* Based on calculations by Santry.⁵

of a guest molecule of trap depth δ is $\Delta w + \delta$, where, for later convenience, δ is negative. The method of finding the stationary states of a mixed crystal is to diagonalize the energy in a basis of localized excitation functions each of which is derived from the functions (2) by substituting guest wave functions for host functions on the appropriate sites. The diagonal elements in the energy matrix are in these cases $\Delta w^1 + D + \delta$ instead of $\Delta w^1 + D$, D being the difference in van der Waals energy between ground and excited states in the crystal lattice. All non-diagonal elements in this localized excitation basis are the same for pure and mixed crystals. The eigenfunctions are not, however, given by expressions (3) because the mixed crystal lacks the full translational symmetry of the host lattice, a fact which deprives \mathbf{k} of significance as a quantum number. However, the Bloch functions (3), with appropriate substitutions of guest for host wave functions, are useful as basis functions for the mixed-crystal problem: they will be referred to as the delocalized basis set, because the functions (3) describe excitation delocalized over the whole crystal. A delocalized basis is convenient in the shallow-trap problem, and the localized basis of functions (2) is used for deep traps.

Finding energy levels and eigenfunctions for the general three-dimensional mixed crystal is a formidable problem, not yet solved in closed form except in special limiting situations. In other cases numerical solutions are available,⁶ but analytical approximations are desirable and only simplified model systems can at present provide them.

IV. The One-dimensional Mixed Crystal

A useful model system is the one-dimensional "crystal". This is a linear array of host molecules with regularly spaced guest molecules. When there is one guest and $m - 1$ hosts in each repeating set the guest concentration is $1/m$, and in the total of n molecules there are n/m sets. The ground- and excited-state wave functions for host and guest are φ , φ^1 , ψ , and ψ^1 respectively, and the transition energies are Δw and $\Delta w + \delta$. The further conditions of the problem are that only nearest-neighbour interactions are included, and that they are taken to be equal for host-host and host-guest pairs. Finally, cyclic boundary conditions will

be applied as usual for crystals, the system being essentially one of n molecules arranged on the circumference of a circle.

The ground-state wave function of the mixed crystals is the product of unexcited free-molecule functions (4)

$$\Phi_G = \varphi_0 \varphi_1 \varphi_2 \cdots \varphi_{m-1} \varphi_m \cdots \varphi_{2m-1} \varphi_{2m} \cdots \varphi_{n-1} \quad (4)$$

The localized excitation wave functions are the analogues of expressions (2), namely (5) for excitation localized on a host

$$\phi_p = \varphi_0 \varphi_1 \cdots \varphi_p^1 \cdots \varphi_{m-1} \varphi_m \cdots \quad (5)$$

$$\Psi_a = \varphi_0 \varphi_1 \cdots \varphi_{m-1} \varphi_m \cdots \varphi_a^1 \cdots \quad (6)$$

molecule and (6) on a guest. The excitation energies of the localized states (5) and (6), both of which are non-stationary states, are $\Delta w + D$ and $\Delta w + D + \delta$, the quantity D being the change in the free-molecule excitation energies in the environment of neighbour molecules.

V. The Molecular-orbital Analogy

The theory of the model system for crystal excitation is analogous to molecular-orbital theory. The localized wave functions (5) and (6) can be written in alternative forms (7) and (8), which

$$\phi_p = \Phi_G \cdot \sigma_p; \quad \sigma_p = \varphi_p^1 / \varphi_p \quad (7)$$

$$\Psi_a = \Phi_G \cdot \tau_a; \quad \tau_a = \psi_a^1 / \psi_a \quad (8)$$

show the localized basis functions as products of the common ground-state wave function and one-site quotient functions σ and τ . Multiplication by the quotient function has the effect of replacing the ground-state wave function by the excited-state wave function of the same molecule. Formally it is necessary to find linear combinations of the quotient functions which, when multiplied by the common factor Φ_G , diagonalize the energy of a crystal hamiltonian with diagonal elements $\Delta w + D$ and $\Delta w + D + \delta$ and molecular interaction energies in the non-diagonal places. The MO analogue is the familiar problem of finding energy levels and molecular orbitals for one electron in an LCAO basis by diagonalizing the energy of a molecular hamiltonian with diagonal

elements α and $\alpha + \delta$ (for an "impurity atom") and by non-diagonal neighbour interactions β . We can treat the functions σ_p and τ_q , or better the products ϕ_p and Ψ_q , as one-site excitation functions analogous to one-site electron functions, *viz.* atomic orbitals. As to the energy terms, one sees that for a crystal hamiltonian $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}$, the sum of the free-molecule hamiltonian and a crystal perturbation \mathbf{V} , the neighbour interaction is

$$(\phi_p | \mathbf{H} | \Psi_q) = (\varphi_p \varphi_p^1 | \mathbf{V} | \psi_q \psi_q^1) \quad (9)$$

depending only on the wave functions on the sites concerned. If this is neglected for all but nearest neighbours the analogy with the simplest form of LCAO MO theory is complete, allowing results in the MO theory of cyclic systems to be taken over. Koster and Slater's work on the theory of *electronic* levels in impure crystals is also of immediate relevance.⁷ In what follows we use the MO notation α , $\alpha + \delta$ and β ; the energy values obtained apply equally to one-electron levels in a set of coupled atomic orbitals and to excitation levels in the one-dimensional crystal. Intensity calculations only have an application to transitions in the mixed crystal.

VI. The Shallow-trap Problem

If the trap depth δ is much less than the neighbour interaction β , a convenient basis is the set of delocalized functions analogous to expressions (3), namely the wave functions for the one-dimensional crystal made up of identical molecules. In the limit $\delta = 0$ these go over into the crystal eigenfunctions for the pure-crystal problem. The basis functions are the functions (10):

$$\Phi_r = n^{-1/2} \sum_{j=0}^{n-1} e^{2\pi i r j / n} \phi_j, \quad r = 0, \pm 1, \dots, n/2 \quad (10)$$

in which the ϕ_j differ from expression (5) by the replacement of the guest wave functions by host functions, appropriately to the pure crystal. The energies of the states (10) depend upon the ordering index r as in expression (11):

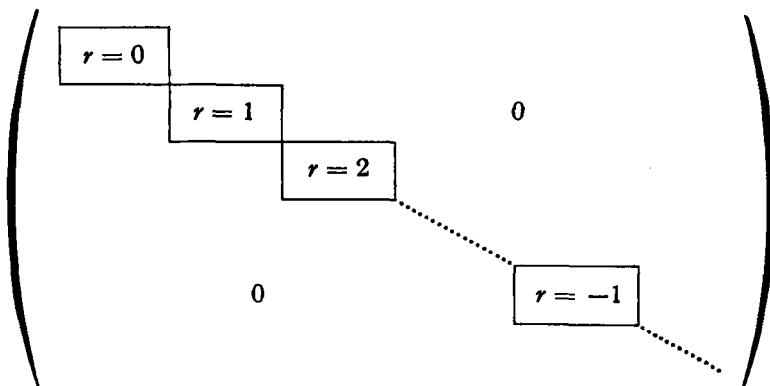
$$E_r = \alpha + 2\beta \cos 2\pi r / n \quad (11)$$

For negative β the band is an *upright* band of energies in the sense that the level $r = 0$ lies lowest, and for positive β it is an *inverted* band with $r = n/2$ lowest.

In the mixed-crystal system, we suppose that for every m th (guest) molecule the transition energy is $\alpha + \delta$ instead of α . In the basis of the delocalized functions (10), the diagonal energies are all changed by addition of a quantity $\delta/m = \sigma$, and non-zero off-diagonal elements appear between pairs of basis functions with indices r differing by multiples of n/m . Thus, for the perturbed hamiltonian \mathbf{H} the energy matrix is composed of elements

$$\begin{aligned} (\Phi_r | \mathbf{H} | \Phi_s) &= \alpha + \sigma + 2\beta \cos 2\pi rs/n, \quad \sigma = \delta/m, \quad \text{for } r = s \\ &= \sigma, \quad s = r \bmod(n/m) \\ &= 0, \quad \text{otherwise} \end{aligned}$$

It can readily be shown that if n/m is odd each of the r values from 0 to $\pm(n-m)/2m$ is associated with a manifold of states of the unperturbed system. If n/m is even the r values are 0, ± 1 , $\pm 2, \dots, n/2m$. The energy matrix may be arranged in blocks



each block being identical in form. The secular equation factors into n/m equations of the form (12), differing only in the ordering index r :

$$\begin{vmatrix} x + \sigma + 2\beta \cos 2\pi r/n & \sigma & \sigma \\ \sigma & x + \sigma + 2\beta \cos 2\pi(r + n/m)/n & \sigma \\ \sigma & \cdot & \cdot \\ & \cdot & \cdot \end{vmatrix} = 0$$

$$x = -E + \alpha \quad (12)$$

the general diagonal element being

$$\alpha + \sigma + 2\beta \cos 2\pi(r + pn/m)/n$$

for $p = 0, \pm 1, \dots, \pm(m-1)/2$ (m odd) and $p = 0, \pm 1, m/2$ (m even). If the coupling constant β is negative (as it is in the analogous MO calculation), the level $r = 0$ lies at the bottom of the band and the lowest mixed-crystal level will come from the $r = 0$ manifold. For positive β the lowest level is that for $r = n/2$: if m is even this also belongs to the $r = 0$ manifold and if m is odd it belongs to the $r = n/2m$ manifold. For even m a sign change of β inverts the $r = 0$ manifold symmetrically about the mean energy; for odd m the sign change sends the $r = 0$ manifold into the $r = n/m$ manifold. The levels are identical in energy in the two cases, but ordered differently with respect to their r values: this change is important in dealing with intensities, as we shall see.

For a set guest concentration m , increasing the total number n of molecules merely adds new manifolds of levels to the secular equation, there being no interactions with existing manifolds. The argument is simplified by this fact and also because for all values of the trap depth δ , and for negative β , the lowest level comes from the $r = 0$ manifold; for positive β the lowest level comes either from the same manifold or from another with the same absolute eigenvalues. It is thus possible to concentrate on the manifold $r = 0$.

VII. Further Consideration of the $r = 0$ Manifold

If the delocalized excitation functions (10) are re-written in the real form (13) the trigonometric coefficients are symmetric or

$$\left. \begin{aligned} \Phi_r^+ &= (2/n)^{\frac{1}{2}} \sum_{j=0}^{n-1} \cos(2\pi r j/n) \phi_j \\ \Phi_r^- &= (2/n)^{\frac{1}{2}} \sum_{j=0}^{n-1} \sin(2\pi r j/n) \phi_j \end{aligned} \right\} \quad (13)^*$$

antisymmetric to reflection at the site $j = 0$. If each function ϕ_j is mapped on to another of the same set by this reflection it is clear that the Φ_r^+ are symmetric and the Φ_r^- antisymmetric. Now perturbation by regularly spaced guest molecules, one of which is at the site $j = 0$, varies as the cosine of $2\pi j/m$ and its multiples. This perturbing potential is symmetric under reflection at $j = 0$, and does not mix the symmetric and antisymmetric functions (13). This simplifies the secular problem in the $r = 0$ manifold, because the lowest level belongs to the symmetric set obtained as solutions to the secular equation in the basis of the first of the expressions (13), namely,

$$\begin{vmatrix} x + \sigma + 2\beta & \sqrt{2}\sigma & \sqrt{2}\sigma \\ \sqrt{2}\sigma & x + 2\sigma + 2\beta \cos 2\pi/n & \sqrt{2}\sigma \\ \sqrt{2}\sigma & \sqrt{2}\sigma & x + 2\sigma + 2\beta \cos 4\pi/n \end{vmatrix} = 0 \quad (14)$$

Moreover, since the antisymmetric functions have the forms (p integral)

$$\left(\frac{2}{n}\right)^{\frac{1}{2}} \sum_j \sin \frac{2\pi j p}{m} \phi_j$$

they vanish at all the guest sites and are unaffected by the perturbation.

VIII. A Limiting Formula for Shallow Traps

For small values of $\sigma = \delta/m$ perturbation methods can be used to approximate to the lowest root of Eq. (12). The energy depression ΔE in the $r = 0$ manifold is given by

$$\Delta E = \frac{\sigma^2}{2\beta} \sum_{p=\pm 1}^{m/2} \frac{1}{1 - \cos 2\pi p/m} = \frac{\sigma^2}{2\beta} \left(\sum_{p=1}^{m/2} \frac{1}{\sin^2 p\pi/m} - \frac{1}{2} \right)$$

* For $r = 0$ and $r = n/2$ the normalizer is $(1/n)^{\frac{1}{2}}$.

In the limit of large m (dilute crystals) this can be shown to approach $\Delta E = \delta^2/12\beta$; already at $m = 4$ the value is within $\frac{1}{18}$ of this limit and at $m = 6$ within $\frac{3}{88}$. The limiting formula may thus be used for all but the most concentrated crystals; but it is valid only for σ small compared with the least of the energy denominators, namely $1 - \cos(2\pi p/m)$, so that it holds for a range of trap depths which narrows as the concentration measured by m^{-1} diminishes. However, in all situations the initial deviation from the unperturbed band is quadratic in the depth δ , just as has been shown for electron traps by Koster and Slater using a different argument.

IX. A Limiting Formula for Deep Traps

At the other limit of δ much larger than β , the delocalized functions (10) are not suitable as a basis because the delocalization is destroyed by the presence of the traps. It is convenient to begin with the localized excitation functions ϕ_j . The secular equation is formally the same as that for the molecular-orbital secular problem based on atomic orbitals, as given in Eq. (15).

$$\begin{vmatrix} \alpha + \delta - E & \beta & 0 & 0 \dots \beta \\ \beta & \alpha - E & \beta & 0 \dots 0 \\ 0 & \beta & \alpha - E & \beta \dots 0 \\ & & & \ddots \\ & & & & \ddots \end{vmatrix} = 0 \quad (15)$$

For sufficiently large δ the depression of the trap level is given by the perturbation expression (16):

$$\Delta E = 2\beta^2/\delta \quad \text{and} \quad E = \alpha + \delta + 2\beta^2/\delta \quad (16)$$

X. Energies for the Example $m = 6$

The general character of the solutions to the energy problem can be shown in a specific example. We choose $m = 6$ because the analogue in molecular-orbital theory, namely the orbitals of benzene and heterocyclic derivatives, is a familiar one. The results hold independently of n , the total number of centres

present. The secular equation (14) is of degree four and readily solved for chosen values of δ . The energy levels are plotted in Fig. 2. The dotted lines show the values given by the limiting formulae.

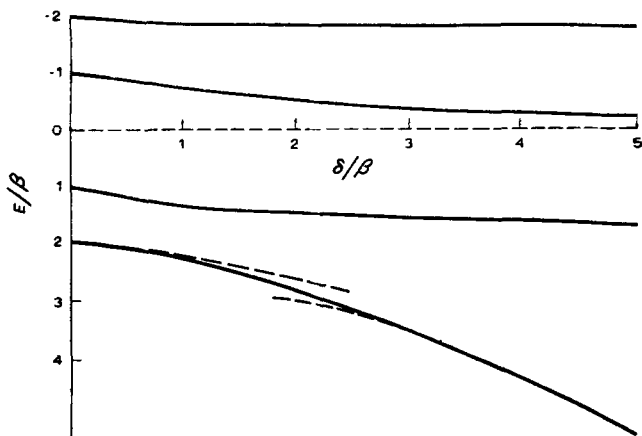


Fig. 2. The energy levels as a function of trap depth δ for the one-dimensional mixed crystal with guest concentration $\frac{1}{6}$. The manifold shown belongs to $r = 0$. The dotted curves are plots of the shallow-trap (left-hand) and deep-trap (right-hand) limiting approximations.

In the limit of large δ the system of m molecules goes into independent sub-systems, one of them the guest molecule alone and the other the residual host consisting of groups of $m - 1$ host molecules separated from other groups by the guests. In the approximation of nearest-neighbour interactions the several residual host groups do not interact. The wave functions for the residual groups are (for $m = 6$)

$$\psi_l = 3^{-\frac{1}{2}} \sum_{j=1}^5 \sin(2\pi lj/12) \phi_j \quad (17)$$

Two of these, namely $l = 2$ and 4 , are identical with the anti-symmetric functions Φ_r^- in Eq. (13) for $r = 1$ and 2 and $n = 6$; the other three, $l = 1, 3$, and 5 , join smoothly with the three upper solutions of Eq. (14) taken to the limit of large β . It is at once obvious that the energies of the functions (17) all lie within the energy range spanned by the original unperturbed system, and

must do so for any m ; this leads to the characteristic result that the levels of the residual system lie wholly within the band of energies of the unperturbed system: only the lowest level of any manifold is displaced outside the band.

XI. Manifolds Belonging to $r \neq 0$

The expression for the depression of the lowest level of a manifold of levels for general r in the shallow-trap limit is

$$\Delta E = \frac{\sigma^2}{2\beta} \sum_{p=\pm 1}^{m/2} \frac{1}{\cos(2\pi r/n) - \cos 2\pi(r + pn/m)/n}$$

which depends upon the total number of molecules n as well as on the index r . If n is taken to be very large, as is reasonable, and r small, the expression for ΔE tends to that for $r = 0$. One level detaches itself from the bottom of the manifold and moves downward with, initially, a quadratic dependence on δ . In the large δ limit it becomes coincident with the $r = 0$ level. In general, one level moves out of the band from each manifold: the several levels converge slowly at intermediate values of δ , and in the large δ limit coalesce to give a set of degenerate pure-guest levels. The number of levels moving out of the band in this way equals the number of guest molecules present. The situation is illustrated in Fig. 3.

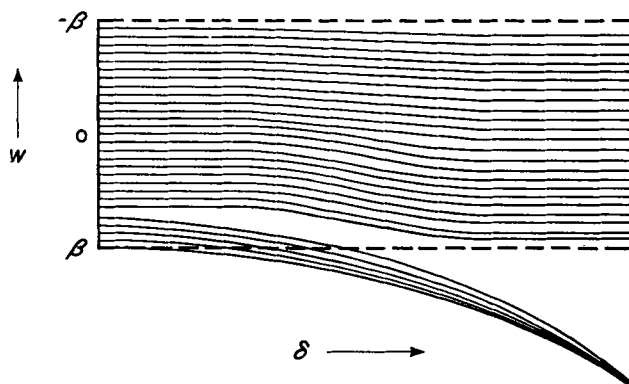


Fig. 3. Schematic diagram of levels in a one-dimensional mixed crystal containing several guest molecules. One level from each manifold moves out of the band, finally coalescing at large trap depths.

XII. Intensities in the One-dimensional Mixed Crystal

The dependence of the energy-level pattern on trap depth is the same for upright and inverted bands. In both, one level from the bottom of each manifold moves out of the band. The similarity does not hold for the intensities of transitions, the spectrum being quite different in the two cases. The difference in spectra originates in the one-dimensional pure crystal because the only allowed transition is to the $r = 0$ level, which is the lowest of an upright band and the highest of an inverted band. In the one case there is a red shift relative to the free-molecule transition (upright band, negative β) or a blue shift (inverted band, positive β).

The transition moment for transitions between the ground state (4) for the pure crystal and the excited state Φ_r , Eq. (10), is given by expression (18):

$$n^{-1} \int \Phi_G \sum_k e\mathbf{r}_k \sum_j \exp(2\pi i r j / n) \phi_j d\tau_k \quad (18)$$

in which $e\mathbf{r}_k$ is the dipole moment operator for electron k , the summation being over all the electrons of the system. If \mathbf{M}_j be written for the single-molecule transition moment, Eq. (19),

$$\int \varphi_j \sum_k e\mathbf{r}_k \varphi_j' d\tau_k = \mathbf{M}_j \quad (19)$$

the moment for the crystal is given by

$$n^{-1} \sum_j \exp(2\pi i r j / n) \mathbf{M}_j \quad (20)$$

the assumption being made that the wavelength of the light is long compared with the dimensions of the crystal. The sum in Eq. (20) is zero except for $r = 0$, the transition being forbidden in all other cases. For $r = 0$ the transition moment is \sqrt{n} times the free-molecule moment and the intensity n times. Thus the intensity per molecule is unchanged, as we expect. The selection rule $r = 0$ corresponds to the familiar restriction to $\mathbf{k} = 0$ in real pure crystals.

The method of treatment of the shallow traps by expanding the perturbed wave functions in a series of the delocalized pure-crystal wave functions Φ_r [Eq. (10)] is also convenient for intensity calculations. Since Φ_0 is the only spectrally active function its

participation in the wave function for any state of the mixed crystal determines the intensity of transitions to that state. That is, the intensity of transitions to any state of the mixed crystal is proportional to the square of the projection of the state onto Φ_0 .

The comparison in Fig. 2 between the position of the lowest energy level and the shallow-trap approximation to it suggests that the approximation is usable to values up to $\delta = 1.5$ or a little greater. In this region of trap depth the expected behaviour is a gradual change from a spectrum with the whole intensity going to the $r = 0$ level of the band ($\delta = 0$) to one having the intensity spread among all levels: for a very deep trap, the trapping molecule has precisely the fraction of the total intensity proportional to its concentration, i.e. $1/m$. Thus in the upright band, to be dealt with first, we have to follow a change of spectrum from that of the pure crystal, with all the intensity in the lowest transition, to the deep-trap limit, with a fraction $1/m$ in the lowest transition.

The $m = 6$ system will again be used as an example. The guest molecules cause the mixing of the lowest ($r = 0$) wave function with three other wave functions derived from $p = \pm 1$, $p = \pm 2$, and $p = 3$, as described in the secular equation (14). If c_1, \dots, c_5 are the coefficients of the basis functions in order of increasing energy in the perturbed lowest state, we have, by perturbation theory for small σ ,

$$\frac{c_2}{c_1} = \frac{\sqrt{2}\sigma}{\beta - \sigma}, \quad \frac{c_3}{c_1} = \frac{\sqrt{2}\sigma}{3\beta - \sigma}, \quad \frac{c_4}{c_1} = \frac{\sigma}{4\beta} \quad (21)$$

The squares of the normalized coefficients c_1^2, \dots, c_4^2 directly give the fractions of the original intensity in transitions to each one of the four states. We may reasonably neglect variations of frequency between the transitions in converting transition moments to intensities because the frequency range of the transitions is small. Typical results are given in Table I.

As the trap is made deeper the intensity spreads more widely over the levels of the band. In treating deep traps it is convenient to begin with the hypothetical limit of the infinitely deep trap, based on the wave functions (17) of the residual host, and to consider transitions to them from the ground state. The transition

TABLE I. Intensity Distribution in the Shallow-trap Limit.
Upright Band, $m = 6$

σ/β	c_1^2	c_2^2	c_3^2	c_4^2
0.05	0.994	5×10^{-3}	5×10^{-4}	< 0.01
0.1	0.973	0.024	0.002	< 0.01
0.2	0.879	0.106	0.009	< 0.01

intensities are proportional to the squares of the projections (22) of each of the functions (17) on the spectrally active function Φ_0 of the delocalized pure crystal set, Eq. (10).

$$\int \psi_l \Phi_0 d\tau = \frac{1}{3\sqrt{2}} \sum_{j=1}^5 \sin(2\pi lj/12) \quad (22)$$

There are zero projections for $l = 2$ and 4 on account of symmetry. The squares of the other projections are given in the last line of Table II. The fractional intensities of transitions to levels of the host add up to five-sixths, the remaining one-sixth appearing in the transition to the trap molecule. For the other cases in Table II intensities have been calculated by perturbation theory based on the residual host wave functions (17) and the free guest wave function.

Values are listed for trap depths from $\delta = 3\beta$ downward, but are of dubious accuracy at the top of this range. The shallow-trap parameter σ of Table I equals $\delta/6$. For trap depths that lie

TABLE II. Intensity Distribution in the Deep-trap Limit.
Upright Band, $m = 6$

δ/β	c_1^2	c_2^2	c_3^2
3.0	0.60	0.40	0.00
3.6	0.47	0.52	0.01
4.2	0.40	0.58	0.01
5.0	0.35	0.63	0.02
8.0	0.27	0.70	0.03
∞	0.167	0.775	0.056

between the limits for shallow- and deep-trap approximations the coefficients c_1, \dots, c_4 must be found by diagonalizing the secular equation. From these results, together with those of Tables I and II, the intensity distribution in the four transitions may be calculated as a function of trap depth. Figure 4 illustrates the way in which the transition to the lowest level gradually weakens, and that to the second level strengthens, as the trap becomes deeper. Other transitions are weak throughout. For

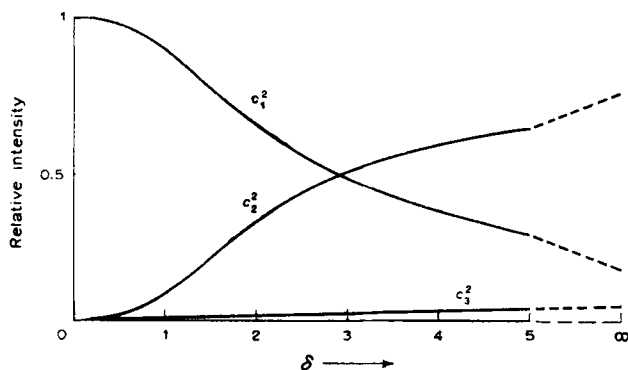


Fig. 4. Relative intensities of transitions in a one-dimensional mixed crystal (upright band). The curve labelled c_1^2 gives the relative intensity in the lowest energy transition. In the limit of large δ this becomes a transition localized in the trapping molecule. c_2^2 and c_3^2 refer to transitions of increasing energy. δ is measured in units of β , the nearest-neighbour coupling energy.

shallow traps the conclusion from these calculations is that there should be one single absorption frequency. For deeper traps there should be two separate absorptions, one to an upper state largely constituted by the excited state of the impurity and the other to a host upper state. The relative strength and the spacing of the transitions depend on the depth of the trap.

In real crystals the $\mathbf{k} = 0$ level will not usually lie at the bottom of the band, but within it (Fig. 1). If spectral activity were induced in the levels below $\mathbf{k} = 0$ in such a situation, the resulting absorption could be observed in the clear region to the red of the $\mathbf{k} = 0$ transition. Absorption to the blue, on the other hand, is obscured. It is thus of great interest to examine a model system

in which the spectrally active level is not at the bottom of the band. The inverted one-dimensional crystal band is of this kind.

For an inverted band the energy levels of the mixed crystal are exactly as shown in Fig. 2, because the secular equation is invariant to the sign of β . We have quite different intensities, because the spectrally active pure-host level now lies at the top of the band. By repeating the calculations using the same methods we get the intensities shown in Fig. 5.

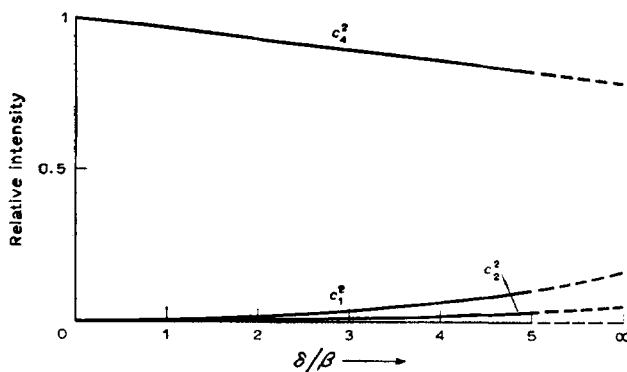


Fig. 5. Relative intensities of transitions in a one-dimensional mixed crystal (inverted band). The curve labelled c_1^2 refers to the lowest energy transition, and c_2^2 and c_4^2 to transitions of higher energy.

In the inverted band a quite different pattern of intensity distribution is to be expected. In the pure crystal the topmost level alone is active; it remains the strongest under all conditions. As the trap is deepened, some intensity moves from the topmost level downward through the band into the bottom level, which breaks out of the band and eventually becomes practically a localized state of the trapping molecule. Thus the presence of guest molecules awakens spectral activity in normally inactive levels, and should enable the extent and character of the pure crystal band structure to be studied experimentally. The point is illustrated in the diagrammatic spectra in Fig. 6, illustrating the transitions in one-dimensional mixed crystals for trap depths from zero (pure crystal) to $\delta = 3.6$. In each case the intensities are adjusted to make the lowest transition have unit intensity: this

corresponds in practical terms to choosing a crystal of convenient thickness. Each level of the pure crystal is to some degree spectrally active in the mixed crystal, and the band structure is in principle available for experimental study. In crystals of lower guest concentration the number of levels in the manifold is greater, and

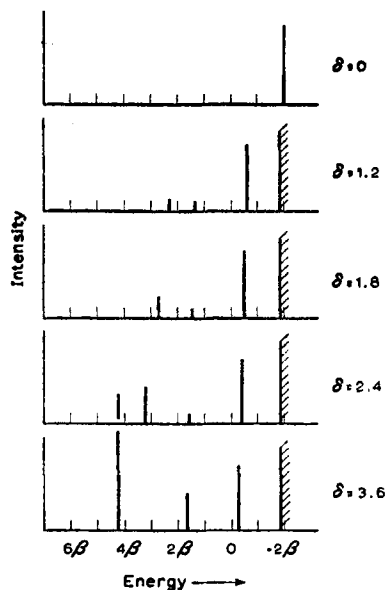


Fig. 6. Schematic absorption spectra of one-dimensional mixed crystals, $m = 6$, with inverted bands, for various trap depths δ . The intensities are adjusted to give equal values in the third transition, except in the top (pure crystal) spectrum. Hatching indicates very intense absorption.

the spectral lines more dense, until in very low concentrations we expect a quasi-continuum of absorption lines. In a sufficiently thick crystal we might expect to find absorption with onset roughly at a frequency for the lowest level of the band and running with varying intensity to a maximum at the top of the band. It must be emphasized that these remarks apply to shallow traps, and to a host with inverted band structure: in an upright band the most intense absorption is at the lowest frequency and any

absorption to higher levels will be obscured by it under practical conditions.

XIII. Applications to Real Crystals

We now mention briefly how these results apply to real three-dimensional crystals in which, as a general rule, the spectrally active levels belonging to zero wave vector lie neither at the top nor at the bottom of the excitation band, but as indicated in Fig. 1. Numerical calculations of special cases show that in the energy region between the bottom of the band and the $\mathbf{k} = 0$ levels the behaviour resembles that of the one-dimensional crystal, in that the guest molecules induce spectral activity in other levels. In particular we may expect absorption to occur at the bottom of the band and with varying intensity up to the pure crystal absorption frequency. The use of mixed crystals may thus allow the spread of the exciton band to be delineated. It seems very probable that impurity-induced absorption lines may already have been observed and mistakenly assigned to transitions in the impurity molecule, instead of the host transitions made spectrally active by host perturbations. Observations of such transitions should provide valuable clues to the band structure, and through that to the structure and dynamics of the crystals.

References

1. For a review see Craig, D. P., and Walmsley, S. H., *Physics and Chemistry of the Organic Solid State*, Interscience, New York, 1963, Ch. 10.
2. McClure, D. S., *J. Chem. Phys.* **22**, 1668 (1954).
3. Choudhury, N. K., and Ganguly, S. C., *Proc. Roy. Soc. (London)* **A259**, 419 (1960).
4. Craig, D. P., and Thirunamachandran, T., *Proc. Roy. Soc. (London)* **A271**, 207 (1963).
5. Santry, D. P., Thesis, University of London, 1962.
6. Craig, D. P., and Philpott, M. R., in press.
7. Koster, G. W., and Slater, J. C., *Phys. Rev.* **96**, 1208 (1954); and earlier papers.

APPLICATIONS OF LIGAND-FIELD THEORY TO COMPLEXES

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Transition-group complexes combine some of the characteristics of "small" molecules, where *a priori* calculations are very difficult, with those of "large" molecules, where they are impossible. The last ten years' progress in this field has been predominantly *inductive*, comparing semi-empirical theories with experimental data and establishing relations within huge classes of compounds. A very good introductory book on ligand-field theory has been written by Orgel,²⁸ a more mathematical book as an extension of Condon and Shortley's *Theory of Atomic Spectra* by Griffith,⁵ and two books^{10,11} and three reviews^{12,13,14} by me. This theory was developed essentially for the interpretation of spectroscopic data though it has actually clarified, in a very general manner, our understanding of chemical bonding in polyatomic, but not too polyatomic, molecules of comparatively high symmetry. Hence it has developed in quite other directions than the older theory of aromatic molecules (cf. reviews in French on MO theory²⁵ and ligand-field theory^{8,30}).

In our attempts to understand chemical bonding and spectroscopic data, we have to live with a series of intrinsic difficulties in quantum mechanics. The most fundamental tendency is perhaps the *approximate invariance of the distribution of perturbed states with regard to symmetry types*. If our approximate wave functions account correctly for the number and approximate order of energy levels and for their symmetry type, they are already doing a good job. We meet such approximations in at least two essential situations. The first occurs for atoms and monatomic ions of spherical symmetry, but it applies to molecules as well. This is the distressing and at the same time encouraging fact that the total wave functions Ψ are definitely very different from single anti-symmetrized Slater determinants (as shown clearly by Watson's Hartree-Fock calculations^{12,35}) and that, at the same

time, the symmetry types of the energy levels observed (S, L, J) are nicely classified by the approximation of well-defined configurations constructed from one-electron wave functions, orbitals ψ , of well-defined symmetry type (here l). The utility of configurations for the *classification* and description of low-lying energy levels is a fact of natural history; it is by no means a demand from group theory. It is of little use to emphasize the purely formal point that only "capital letter" quantum numbers of the total system are determined by group-theoretical conditions. Any (of the few surviving) atomic spectroscopists tell us that the group theorist would never be able to predict which symmetry types would be represented among the lower energy levels if he was not aided by some configurational book-keeping. There is no doubt that exactly the same situation occurs in molecules with regard to the symmetry types of energy levels (S and Γ_n , also called Λ in the linear molecules) classified by MO configurations, each orbital having a well-defined γ_n (called λ in the linear symmetries).

Moreover, in molecules, another essential case of approximate invariance occurs. This is the question of relevant and irrelevant symmetry components.^{15,21} One might modestly think that the symmetry of a molecule, once the nuclear positions are prescribed, is an entirely objective quantity.

However, the presence of the two-electron operator of inter-electronic repulsion in the Hamiltonian disturbs this simple picture. It may be more convenient to neglect some of the symmetry elements of the actual system (this may be especially true of the translational symmetry of crystals producing energy bands as orbitals) or to adopt a higher symmetry to which the actual molecule is only an approximation. The point is that the MO configurations $\gamma_n^a \gamma_m^b \dots$ thus arbitrarily defined may be relatively better approximations to the total wave function Ψ than the strict configurations, which suffer from larger non-diagonal elements of the two-electron operator.

A common instance of the approximate invariance is the occurrence of *chromophores*, i.e., small atomic clusters having identifiable spectral properties.^{21,24} The empirical theory of organic dyes contains many such examples, e.g., the carbonyl group R_2CO , the nitro group RNO_2 or, for that matter, the six carbon

atoms in a benzene ring or C_{10} in a naphthalene derivative. In these formulae, R indicates an atom bound by an "innocent" σ -bond to the chromophore. In carbon compounds especially, it is quite evident that chromophores with internal fractional bond-orders can be effectively separated by σ -bonded chains, a most striking example being compounds³¹ of the type $C_{10}H_7(CH_2)_n C_{14}H_9$, where light quanta manifestly absorbed in the naphthalene part produce fluorescence in the anthracene group for $n = 1, 2, 3$, whereas this process is much less probable for separated molecules in solution. Daudel³ discussed the difference between aliphatic chains where inductive effects are rapidly and monotonically attenuated as a function of distance and chains with fractional bond-orders where large and alternating effects occur. At this summer school, Mason has discussed simpler chromophores and the perturbation from neighbour groups. Actually, the MO treatment starting from the individual chromophores recognizes the elements of relevant symmetry only, which are frequently much higher than that of the complete molecule.

Inorganic chromophores often have a very high micro-symmetry. Good examples are the octahedral clusters MX_6 and the regular tetrahedral or square-planar clusters MX_4 . The central atom M is here surrounded by ligand atoms X, which are either monatomic species (such as F^- , Cl^- , Br^- , I^- , O^{2-}) or they belong to molecules (N of NH_3 or C_5H_5N , and O of H_2O or OH^-). In the case of multidentate ligands, one molecule may furnish several X atoms (thus the O from CO_3^{2-} or $(COO)_2^{2-}$, two N's from $NH_2CH_2CH_2NH_2$, two S's from $(C_2H_5O)_2PS_2^-$ or $(C_2H_5)_2NCS_2^-$). The characteristic feature of high micro-symmetry is the existence of *degenerate orbitals* which necessarily, for group-theoretical reasons, have the same one-electron operator energy. Spherical symmetry is the example *par excellence*: $(2l + 1)$ different orbitals characterized by angular functions which are linear combinations of homogeneous polynomials

$$x^a y^b z^c / r^l \text{ with } l = a + b + c \quad \text{and} \quad r^2 = x^2 + y^2 + z^2 \quad (1)$$

forming each shell. If the three Cartesian coordinate axes are equivalent in the molecule (e.g. octahedral and tetrahedral

symmetry), sets of three degenerate orbitals can occur. Thus, the lower values of l remain partly degenerate:

$$\begin{array}{ll}
 \text{s-shell } l = 0: & 1 \\
 \text{p-shell } l = 1: & x/r, y/r, z/r \\
 \text{d-shell } l = 2: & \text{one sub-shell: } (2z^2 - x^2 - y^2)/r^2, (x^2 - y^2)/r^2 \quad (2) \\
 & \text{another sub-shell: } xy/r^2, xz/r^2, yz/r^2
 \end{array}$$

It is quite evident that the three orbitals forming the second sub-shell for $l = 2$ remain degenerate in octahedral symmetry, and it can be proved in a few minutes that the first two d -orbitals also remain degenerate. If we consider tetragonal symmetry, say in *trans*-MX₄Y₂ or square-planar MX₄, only two of the Cartesian coordinate axes are equivalent. Let us call them x and y . Then, among the p -orbitals, x/r and y/r are degenerate and different from z/r , whereas among the d -orbitals, the only sub-shell to remain degenerate is xz/r^2 and yz/r^2 .

One of the most conspicuous consequences of the existence of sets of e degenerate orbitals is the occurrence of energy levels with positive and varying values of the total spin quantum number S . In the case of a half-filled set, S of the ground state is $e/2$, whereas other energy levels of the same configuration assume the values $S = (e/2) - 1, (e/2) - 2, \dots$. Inorganic chemists accustomed to the perfect stability of compounds with high values of $S = \frac{3}{2}, 2, \frac{5}{2}, 3, \frac{7}{2}$ interpret this in terms of Hund's rule that *if* a configuration can show several values of S , the *highest* value corresponds to the lowest energy. Actually it is possible to prove (at least in the cases $l = 1, 2, 3$) that the average value of the interelectronic repulsion energy of all energy levels having a given value of S of the configuration l^e contains the contribution^{12, 16}

$$D[\langle S(S+1) \rangle - S(S+1)] \quad (3)$$

$\langle \rangle$ denoting the average value of $S(S+1)$ in the configuration and D being a *spin-pairing energy parameter*. As with all other parameters of interelectronic repulsion, D is inversely proportional to the average radius $\langle r \rangle$ in a set of "scaled" radial functions. We call the energy difference between the two d -sub-shells in

Eq. (2) Δ , though the symbols $(E_1 - E_2)$ and $10Dq$ are used by various authors. Δ has turned out to be positive in octahedral clusters, MX_6 , and negative in tetrahedral clusters, MX_4 . The competition between the one-electron promotion energy, expressed in terms of Δ , and the spin-pairing energy, expressed as a multiple of D from Eq. (3), explains the occurrence of high-spin and low-spin complexes. Thus, five electrons in an octahedral chromophore MX_6 (the lower sub-shell of Eq. (2) is denoted t_{2g} or even γ_5 , the higher sub-shell e_g or even γ_3) have the choice between the spin values $S = \frac{3}{2}(t_{2g}^3 e_g^2)$ and $\frac{1}{2}(t_{2g}^5)$. If we neglect the constant contribution $\langle S(S+1) \rangle$ from Eq. (3), the two energies can be written:

$$\text{high-spin: } -\frac{3}{4}\Delta, \quad \text{low-spin: } -2\Delta - \frac{3}{4}D \quad (4)$$

Hence, the low-spin form will be the most stable if Δ is larger than $4D$. By the same token, six electrons in the partly filled shell prefer the high-spin $S = 2(t_{2g}^4 e_g^2)$ or low-spin $S = 0(t_{2g}^6)$ condition according to which of the two energies,

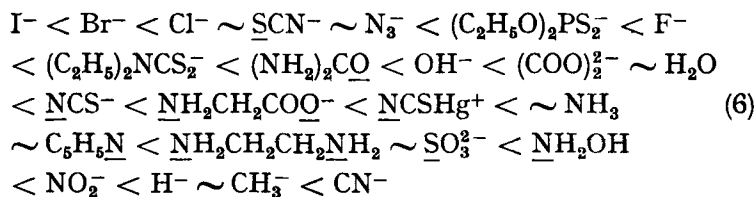
$$\text{high-spin: } -6D, \quad \text{low-spin: } -2\Delta, \quad (5)$$

is the lowest, i.e., the complexes become low-spin if $\Delta > 3D$.

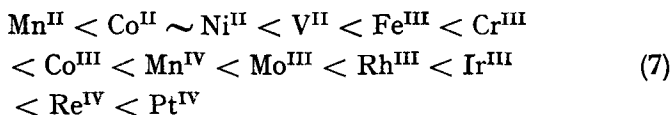
This explains why d^8 complexes more readily become low-spin than d^5 complexes. Since we shall see that $4d$ and $5d$ group complexes have at the same time larger Δ and smaller D values than similar $3d$ group complexes, we shall understand why low-spin behaviour is nearly universal in the two latter transition groups, whereas it is rather the exception in the iron group.

The detailed interpretation of the transitions in the two sub-shells of an octahedral chromophore MX_6 is made by comparison with an Orgel diagram²⁷ (having Δ as variable) or a Tanabe-Sugano diagram³³ (having Δ/B as variable, B being an inter-electronic repulsion parameter $\sim 0.15D$) as discussed in Orgel's lectures. We can say quite generally that such a chromophore is characterized by three parameters: Δ and D (or B) derived from transitions in the partly filled shell, and the optical electronegativities χ_{opt} derived from the electron-transfer spectra where an electron jumps from a filled MO to the partly filled (or empty, such as WCl_6 or MoF_6) shell.

The *spectrochemical series* is the variation of Δ as a function of the ligands for a definite central ion (the binding atom(s) of the more complicated ligands are underlined):



and the variation of Δ as a function of central ions for a definite ligand is:



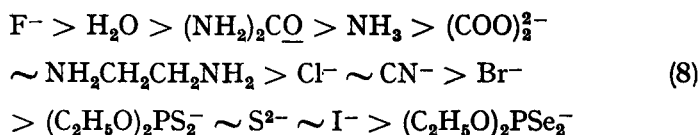
Whereas it has now become clear that Δ cannot be calculated directly from first principles, it is possible to give some qualitative reasons for the variation. It is evident that the electrostatic model, considering the monatomic chromophore M perturbed by an external field representing the ligands, is insufficient to explain the variation in Eq. (6), where anions, neutral molecules and even a cation are completely mixed. From the point of view of MO theory, the main origin of Δ is the σ -anti-bonding character of the upper sub-shell of MX_6 . Actually, as first pointed out by Van Vleck,³⁴ the ligands are influenced by the approximately linear symmetry of the bond region MX . Hence, the orbitals of X can be approximately characterized by the quantum numbers $\lambda = 0(\sigma)$, $\lambda = 1(\pi)$ and so on. If the atom X is a closed-shell halide or oxide ligand, the outermost p shell divides into two degenerate π -orbitals and one σ -orbital. The six σ -orbitals of the cluster MX_6 , directed along the coordinate axes towards M , transform as the six highest orbitals of Eq. (2) having the symmetry types $\gamma_n = a_{1g}$, t_{1u} , and e_g . Consequently, the empty s - and p -orbitals of M and the set of two d -orbitals forming the higher sub-shell become the σ -anti-bonding components of a set of six σ -bonding orbitals filled by twelve electrons.

The main trend of Eq. (6) is that Δ increases for decreasing atomic radius of X, which would be compatible with effects of σ -anti-bonding on the partly filled shell. However, the large number of sulphur-containing ligands¹⁹ is included in Eq. (6) to demonstrate the effects of π -anti-bonding on the partly filled shell. Among the twelve π -orbitals of MX_6 , three transform group-theoretically as the lower sub-shell of Eq. (2) (for nearly complete lists of γ_n see Eisenstein⁴) and hence, as first pointed out by Orgel²⁶ in 1955, Δ is essentially the *difference* between the σ -anti-bonding and the π -anti-bonding effects on the partly filled shell.

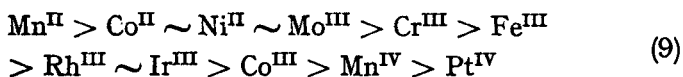
The ligands with only one lone pair, such as NH_3 , SO_3^{2-} , NO_2^- , CH_3^- , and H^- , have only σ -anti-bonding effects and hence the largest values of Δ in Eq. (6). On the other hand, when nitrogen (N_3^- , NCS^-) and sulphur ($(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$ and $(\text{C}_2\text{H}_5)_2\text{NCS}_2^-$) have more than one lone pair^{17, 19} available for complex formation, the resulting π -anti-bonding influence (also found in all four halides) decreases Δ .

When the values of interelectronic repulsion parameters such as Racah's linear combination B , or D , are determined in complexes, they are invariably found to be smaller than in the corresponding gaseous ion M^{2+} . This is called the *nephelauxetic* (cloud-expanding) effect³² because decreased values of B and D correspond to a larger average radius of the partly filled shell. As discussed by Orgel,²⁷ Tanabe and Sugano,³³ Owen,²⁹ and myself,⁷ the phenomenon can be ascribed to two different effects: the *central-field covalency*, since the central ion is invaded by electrons from the ligands forming σ -bonds and hence exhibits a lower effective charge than the corresponding gaseous ion, and the *symmetry-restricted covalency*, since the σ -anti-bonding sub-shell by its mere delocalization has a smaller interelectronic repulsion even with an electron of the other, less delocalized, sub-shell.

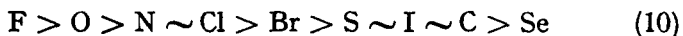
The *nephelauxetic series*¹⁴ of ligands, keeping the central ion constant, is



whereas the function of central ions for a definite ligand is

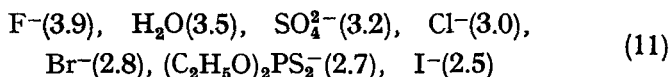


There is a close connection between the usual chemical feeling of how complexes containing relatively reducing ligands and relatively oxidizing central ions tend to form the most covalent bonds and the sequence expressed in the nephelauxetic series. Actually, the Pauling electronegativities fall in the order



and electronegativity increases along the series of Eq. (9). For a definite metallic element, the electronegativity increases strongly with the oxidation number and is therefore larger for Mn^{IV} than for Mn^{II} and larger for Co^{III} than for Co^{II} .²⁰

However, spectroscopic investigations have revealed an even more direct way of measuring a quantity closely related to the electronegativities. Most electron-transfer bands are caused by transitions from filled MO's predominantly localized on the ligands X, say of MX_6 , to one of the two sub-shells mainly concentrated on M. It was observed that these absorption bands shift to lower wave numbers when the electronegativity of X decreases.⁹ This shift is so regular in all the MX_6 studied that it is possible^{11,13} to define *optical electronegativities*, x_{opt} , of



and a set of x_{opt} of the lowest sub-shell (not σ -anti-bonding) of M defined in such a way that

$$E_{\text{corr.}} = (30 \text{ kK})[x_{\text{opt}}(\text{X}) - x_{\text{opt}}(\text{M})] \quad (12)$$

where $E_{\text{corr.}}$ is the wave number of the first Laporte-allowed, strong electron-transfer band corrected for the influence of the spin-pairing energy of Eq. (3). This is usually a rather small correction, D being from some 2–3 kK (in the $4d$ and $5d$ groups) to some 4–6 kK (in the $3d$ group). The constant 30 kK (30,000 $\text{cm}^{-1} = 3.7 \text{ eV} = 85 \text{ kcal/mole}$) in Eq. (12) is chosen to give

values of x_{opt} in Eq. (11) close to the Pauling electronegativities of the halogens.

As partly seen from Table I, the order of increasing x_{opt} of the central ions is

$$\begin{aligned} \text{Mn}^{\text{II}} &< \text{Mo}^{\text{III}} < \text{Cr}^{\text{III}} \sim \text{Co}^{\text{II}} < \text{Os}^{\text{III}} < \text{W}^{\text{VI}} \\ &< \text{Mo}^{\text{VI}} \sim \text{Ru}^{\text{III}} \sim \text{Ni}^{\text{II}} < \text{Os}^{\text{IV}} \sim \text{Ir}^{\text{III}} \\ &< \text{Co}^{\text{III}} \sim \text{Cu}^{\text{II}} \sim \text{Rh}^{\text{III}} < \text{Ru}^{\text{IV}} \sim \text{Ir}^{\text{IV}} \\ &< \text{Rh}^{\text{IV}} \sim \text{Os}^{\text{VI}} < \text{Pt}^{\text{IV}} < \text{Ir}^{\text{VI}} < \text{Pt}^{\text{VI}} \end{aligned} \quad (13)$$

In the case of Ni^{II} , Ir^{III} , Co^{III} , Cu^{II} , Rh^{III} , and Pt^{IV} , the lower sub-shell is filled, and one only sees electron-transfer bands at a wave number Δ larger than suggested by Eq. (12).

Oxo complexes, whether regular tetrahedral,² such as CrO_4^{2-} , MnO_4^- , MoO_4^{2-} , RuO_4 , or substituted octahedral,^{1,6} such as $\text{VO}(\text{H}_2\text{O})_5^{2+}$, MoOCl_5^{2-} , or $\text{RuO}_2\text{Cl}_4^{2-}$, can be treated only with much greater difficulty by the theory of optical electronegativities, and it is not possible to give a well-defined value for O^{2-} in Eq. (11). The main reason is that this ligand has a very strong π -anti-bonding influence on the partly filled shell and, hence, the central ion seems to have a lower value of x_{opt} than in the other types of complexes.

Recently, it has been possible¹⁶ to determine x_{opt} of the lanthanide complexes containing a partly filled $4f$ shell. The corrections for spin-pairing energy in Eq. (3) are rather large since $D \sim 6.5$ kK, and certain corrections for relativistic effects (spin-orbit coupling) also have to be made. The $E_{\text{corr.}}$ observed correspond to $x_{\text{opt}} = 0.8$ for Sm^{III} , 0.95 for Eu^{III} , 1.45 for Tm^{III} , 1.6 for Yb^{III} , 2.7 for Nd^{IV} , and 3.7 for Dy^{IV} , a much larger variation with increasing oxidation number than found in any other transition group.¹⁸ The lanthanides represent a very characteristic case of monatomic chromophores, M , the distribution of energy levels being nearly the same as in the corresponding gaseous ions. The small "ligand-field" splittings found can be interpreted nicely in terms of up to seven slightly different one-electron energies of the $4f$ shell. I do not believe that the main origin of these energy differences is an electrostatic perturbation, but rather again very weak covalent bonds. The lanthanides exhibit a weak nephelauxetic effect, giving about

TABLE I. Wave Numbers in kK (1000 cm^{-1}) and Spectrochemical and Nephelauxetic Parameters. The nephelauxetic ratio¹⁴ is derived from spin-allowed transitions (β_{ss}). The optical electronegativity, χ_{opt} , is determined for the lowest sub-shell

	Internal transitions in the partly filled shell		First Laporte- allowed electron- transfer band	Δ	B	β_{ss}	χ_{opt}
	Spin-allowed	Spin-forbidden					
$3d^3$	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	17.4, 24.6, 37.8	15.0	17.4	0.72	0.79	—
	$\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$	17.5, 23.9	14.35	17.5	0.62	0.68	—
	CrF_6^{3-}	14.9, 22.7, 34.4	15.7, 16.4	15.2	0.82	0.89	—
	$\text{Cr}(\text{NH}_3)_6^{3+}$	21.55, 28.5	15.3	21.6	0.65	0.71	—
	$\text{Cr}(\text{CN})_6^{3-}$	26.7, 32.2	—	38.0	0.53	0.58	—
	$\text{Cr}(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_3$	14.3, 18.9	13.1, 13.6	28.8	0.41	0.45	—
	MnF_6^{3-}	21.75, 28.2	16.3	—	0.60	0.56	—
$3d^6$	$\text{Co}(\text{H}_2\text{O})_6^{3+}$	16.6, 24.9	—	18.2	0.67	0.61	—
	$\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$	16.5, 23.8	—	18.0	0.54	0.49	—
	$\text{Co}(\text{NH}_3)_6^{3+}$	21.0, 29.5	13.0	22.9	0.62	0.56	—
	$\text{Co}(\text{CN})_6^{3-}$	32.4, 39.0	—	33.5	0.46	0.42	—
	$\text{Co}(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_3$	13.55, 19.0	—	24.6	0.40	0.36	2.3
$3d^8$	$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	8.5, 13.5, 25.3	15.4, 22.0	—	0.94	0.89	—
	KNiF_6	7.3, 12.5, 23.7	15.3, 21.0	—	0.96	0.91	—
	$\text{Ni}(\text{NH}_3)_6^{2+}$	10.8, 17.5, 28.2	13.15	—	0.89	0.84	—
$4d^3$	MoCl_6^{3-}	19.15, 23.9	9.65, 14.8	45	0.44	0.73	1.7
$4d^5$	RuCl_6^{3-}	19.0	—	28.7	—	—	2.1
	RhCl_6^{3-}	—	—	12.0	—	—	2.6

4d ⁶	Rh(H ₂ O) ₆ ³⁺	25.5, 32.8	—	50	27.0	0.51	0.71	—
	RhCl ₆ ³⁻	19.3, 24.3	14.7	39.2	20.3	0.35	0.48	2.3
	RhBr ₆ ³⁻	18.1, 22.2	—	30.1	19.0	0.28	0.39	2.3
	Rh(NH ₃) ₆ ³⁺	32.7, 39.1	—	—	34.1	0.43	0.60	—
	Rh(CN) ₆ ³⁻	44.1, 47.6	—	—	45.0	(0.23)	(0.32)	—
	Rh(S ₂ P(OC ₂ H ₅) ₂) ₃	21.3, 24.4	—	31.2	22.0	0.21	0.29	2.3
	PdCl ₆ ²⁻	20.8	—	29.4	—	—	—	2.7
5d ⁰	WF ₆	—	—	57.1	—	—	—	2.0
	WCl ₆	—	—	26.4	—	—	—	2.0
5d ²	OsF ₆	—	4.3, 8.5, 17.3	35.7	—	—	—	2.6
5d ³	ReF ₆ ³⁻	32.8	10.8, 11.4, 17.7, 18.9	—	32.8	—	—	—
	ReCl ₆ ³⁻	27	9.5, 14.2, 15.7	35.6	27	—	—	2.0
	ReBr ₆ ³⁻	—	9.3, 13.2, 15.1	28.4	—	—	—	2.0
	IrF ₆	—	6.4, 9.1, 12.6, 15.6,	35.0	—	—	—	2.9
5d ⁴	OsCl ₆ ²⁻	—	10.8, 11.7, 17.2	27.0	—	—	—	2.2
	OsBr ₆ ²⁻	—	10.6, 11.3, 16.1	20.4	—	—	—	2.2
	PtF ₆	—	5.8, 11.9, 12.6, 15.9	25	—	—	—	3.2
5d ⁵	OsCl ₆ ³⁻	—	—	35.4	—	—	—	1.9
	IrCl ₆ ³⁻	—	—	20.5	—	—	—	2.35
	IrBr ₆ ³⁻	—	—	14.9	—	—	—	2.35
5d ⁶	IrCl ₆ ³⁻	24.1, 28.1	17.9	48.5	25.0	0.30	0.46	2.2
	IrBr ₆ ³⁻	22.4, 25.8	16.8	36.8	23.1	0.25	0.38	2.25
	Ir(S ₂ P(OC ₂ H ₅) ₂) ₃	26.2, 28.6	21.2	37.4	26.6	0.16	0.24	2.3
	PtF ₆ ²⁻	31.5, 36.4	24.4	—	33.0	0.38	0.53	—
	PtCl ₆ ²⁻	28.3, —	22.1	38.2	29	—	—	2.6
	PtBr ₆ ²⁻	—	—	31.8	—	—	—	2.6

1% smaller values of the parameters of interelectronic repulsion in complexes and solid compounds of the heavy halides compared to the aquo and fluoro complexes.¹¹ The 5*f*-group complexes have somewhat larger, but not very much larger, "ligand-field" effects than the lanthanides, and comparable or slightly larger nephelauxetic effects. According to private communications from Dr. J. Ryan, Hanford, it has recently been possible to estimate values of x_{opt} in various central ions, such as 1.5 for U^{IV}, 1.75 for Np^{IV} and 2.05 for Pu^{IV} [*Mol. Phys.* 7, 17 (1963)].

Other cases of approximately monatomic chromophores occur in 4*f* → 5*d* transitions now known in Sm^{II}, Eu^{II}, Tm^{II},²³ Yb^{II}, Ce^{III}, Pr^{III}, and Tb^{III}.¹⁶ (The half-filled shell effect expressed by Eq. (3) is very conspicuous in this distribution of known species.) 5*f* → 6*d* transitions are known in U^{III}, Np^{III}, Pu^{III}, Pa^{IV}, U^{IV}, Np^{IV}, and Pu^{IV}. 5*s* → 5*p* transitions are known in complexes of Sn^{II} and Sb^{III} and 6*s* → 6*p* in Tl^I, Pb^{II}, and Bi^{III}. The halide ions in solvents of not too high electron affinity and in crystals of alkali metal halides show absorption bands which to a certain approximation can be described as 3*p* → 4*s*(Cl), 4*p* → 5*s*(Br), and 5*p* → 6*s*(I).

Fundamentally, I am not very optimistic about actual *a priori* calculations of energy levels of this very wide class of molecules. It is only the "approximate invariance" which supports the semi-empirical, or as they are often called now, phenomenological descriptions. It is quite clear that the reason for the success of the ligand-field theory is *not* any strong tendency to electrovalent bonding; the classification remains adequate even in a region of very definitely covalent complexes such as Co[S₂P(OC₂H₅)₂]₃ and RhCl₆³⁻. Rather, the reason is Nature's most incredible indulgence with respect to the "approximate invariance . . ." of the *one-electron approximation*. By the same token as we talk freely of one valency electron in an isolated sodium atom or two valency electrons in magnesium, we need in ligand-field theory the self-confidence to talk of a well-defined integral number of electrons in the partly filled shell. We imagine these electrons occupy orbitals which are the eigenfunctions of an appropriate core field, $U(x,y,z)$, of the same symmetry as the chromophore, just as the Hartree-Fock orbitals are eigenfunctions of a central field, $U(r)$, of spherical symmetry. If the word "ligand field" has any meaning, it has to be

considered as the difference, $U(x,y,z) - U(r)$, between quantities occurring in the Hamiltonian, and not simply as an external electrostatic field. We have no need to pose the condition that the eigenfunctions should be localized in the central atom alone; we hardly get any conceptual advantage from such a restrictive assumption as long as we remain in the one-electron approximation.

It is possible to make an analysis²³ of the various models one may apply to the octahedral chromophore MX_6 . For instance, the conservation of the angular variation expressed in Eq. (2) together with a radial function which is not only adapted to a smaller effective charge of the central atom than the oxidation number but which may show nodes before arriving in the ligand atoms illustrating the anti-bonding character of the partly filled shell is still compatible with the Tanabe-Sugano diagrams. It is worth remarking that the actual extent of the nephelauxetic effect¹⁴ suggests that the partly filled shell in nearly all complexes is localized somewhat more on the central atom than on the surrounding ligand atoms.

However, if one wishes to attempt to make actual calculations of the MO's of the simpler chromophores, I suspect that the most sensible approach is to use the LCAO model in the way elaborated by Wolfsberg and Helmholz.³⁶ This model has recently been used by Ballhausen and Gray¹ to investigate $VO(H_2O)_5^{3+}$. One of the fundamental difficulties is that the diagonal elements of the energy in this model are very steep functions of the atomic charges.¹¹ Since the atomic charges rearrange strongly under the delocalization of the individual MO's, it is not all that clear that the whole process by iteration is convergent. This is, in my opinion, a more serious problem than the presence of non-diagonal elements in the model, which admittedly also vary to some extent during the iteration but which have a much more clear-cut function in expressing the comparatively weak chemical bonding effects. The reason for this deviation from a simple problem of perturbation theory is the intricate mixture of one-electron and two-electron operator quantities in the "orbital energies" of such a model. It would be worth studying to what extent the semi-empirical quantities x_{opt} may be reproduced by such a model; it is evident that the spectrochemical and nephelauxetic series can be qualitatively accounted for.

Our conclusion today is that ligand-field theory is essentially the one-electron approximation used for the classification of the energy levels of inorganic chromophores.

Note Added in Proof

A certain revival of the ligand-field theory has recently taken place through the introduction of the *angular overlap model* [Jørgensen, C. K., Pappalardo, R., and Schmidtke, H. H., *J. Chem. Phys.* **39**, 1422 (1963); Schmidtke, H. H., *Z. Naturforsch. Teil a*, in press; Schäffer, C. E., and Jørgensen, C. K., submitted to *Mol. Phys.*] and the observation that this model, somewhat related to the Hückel theory but utilizing the hydrogenic form of the angular *l*-functions in Eq. (1), has the same consequences as a contact term consisting of a singular potential acting close to each ligand nucleus. This model permits the description of σ - as well as π - and δ -anti-bonding effects. The ratio $-4/9$ between the values of Δ in tetrahedral and octahedral chromophores MX_4 and MX_6 with the same M—X distances, which has frequently been used as an argument for the electrostatic model, follows immediately from the much more general angular overlap model.

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References

1. Ballhausen, C. J., and Gray, H. B., *Inorganic Chemistry* **1**, 111 (1962).
2. Carrington, A., and Jørgensen, C. K., *Mol. Phys.* **4**, 395 (1961).
3. Daudel, R., *Structure Électronique des Molécules*, Gauthier-Villars, Paris, 1962.
4. Eisenstein, J. C., *J. Chem. Phys.* **25**, 142 (1956).
5. Griffith, J. S., *The Theory of Transition-Metal Ions*, Cambridge University Press, 1961.
6. Jørgensen, C. K., *Acta Chem. Scand.* **11**, 73 (1957).
7. Jørgensen, C. K., *Discussions Faraday Soc.* **26**, 110 (1958).
8. Jørgensen, C. K., *J. Chim. Phys.* **56**, 889 (1959).
9. Jørgensen, C. K., *Mol. Phys.* **2**, 309 (1959).
10. Jørgensen, C. K., *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, Oxford, 1962. (U.S. distributor: Addison-Wesley, Inc., Reading, Mass.)

11. Jørgensen, C. K., *Orbitals in Atoms and Molecules*, Academic Press, London, 1962.
12. Jørgensen, C. K., *Solid State Phys.* **13**, 375 (1962).
13. Jørgensen, C. K., *Advan. Chem. Phys.* **5**, 33 (1963).
14. Jørgensen, C. K., *Progr. Inorg. Chem.* **4**, 73 (1962).
15. Jørgensen, C. K., *Physica Status Solidi* **2**, 1146 (1962).
16. Jørgensen, C. K., *Mol. Phys.* **5**, 271 (1962).
17. Jørgensen, C. K., *Mol. Phys.* **5**, 485 (1962).
18. Jørgensen, C. K., *Mol. Phys.* **6**, 43 (1963).
19. Jørgensen, C. K., *J. Inorg. Nucl. Chem.* **24**, 1571 (1962).
20. Jørgensen, C. K., *Acta Chem. Scand.* **16**, 2017 (1962).
21. Jørgensen, C. K., Lectures given at the Battelle symposium, "Local Properties of Perfect Crystals," held in Geneva, July, 1962; *Inorganic Complexes*, Academic Press, London, 1963; and *Experientia Suppl.* **9**, 98 (1964).
22. Jørgensen, C. K., Lectures given at the NATO Summer School on "Ligand Field Theory" held in Konstanz-am-Bodensee, September, 1962. In press at Springer Verlag.
23. Kiss, Z. J., *Phys. Rev.* **127**, 718 (1962).
24. Mason, S. F., *Quart. Rev.* **15**, 287 (1961).
25. Mulliken, R. S., *J. Chim. Phys.* **46**, 497 (1949).
26. Orgel, L. E., *J. Chem. Phys.* **23**, 1819 (1955).
27. Orgel, L. E., *J. Chem. Phys.* **23**, 1824 (1955).
28. Orgel, L. E., *Transition-Metal Chemistry*, Methuen, London, 1960.
29. Owen, J., *Proc. Roy. Soc. (London)* **A227**, 183 (1955).
30. Poulet, H., *J. Chim. Phys.* **54**, 258 (1957).
31. Schnepf, O., and Levy, M., *J. Am. Chem. Soc.* **84**, 172 (1962).
32. Schäffer, C. E., and Jørgensen, C. K., *J. Inorg. Nucl. Chem.* **8**, 143 (1958).
33. Tanabe, Y., and Sugano, S., *J. Phys. Soc. Japan* **9**, 753 and 766 (1954).
34. Van Vleck, J. H., *J. Chem. Phys.* **3**, 803 (1935).
35. Watson, R. E., *Phys. Rev.* **118**, 1036 (1960).
36. Wolfsberg, M., and Helmholz, L., *J. Chem. Phys.* **20**, 837 (1952).

PART II

**CHEMICAL AND BIOCHEMICAL
ACTIVITY**

CHEMICAL REACTIVITY

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I. GENERAL PRINCIPLES

Chemical reactivity depends on the differences in free energy between pairs of closely related systems. In the case of a reversible reaction, the equilibrium constant (K) is determined by the difference (ΔF) in free energy between the reactants and the products:

$$-RT \log K = \Delta F \quad (1)$$

In the case of an irreversible reaction, the rate constant (k) is determined by the difference in free energy (ΔF^\ddagger) between the reactants and the transition state:

$$-RT \log k = \Delta F^\ddagger \quad -RT \log (kT/h) \quad (2)$$

These free energy differences can be expressed in terms of differences in heat content (H) and entropy (S):

$$\Delta F = \Delta H - T\Delta S; \quad \Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3)$$

Our problem is to determine differences in heat content and entropy between such pairs of systems. The problem is simplified in practice by the fact that the systems in a pair are invariably similar; reactions involving extensive reorganization of the atoms in the reactants normally occur too slowly to be significant. The majority of reactions that take place at a reasonable rate under homogeneous conditions involve the rupture and/or formation of one bond, and very few reactions involve the simultaneous rupture or formation of more than two bonds.

The entropy of a molecule depends in a complicated way on its modes of vibration and rotation; it can be estimated from first principles only for a few very simple molecules. In other cases the entropy may be estimated approximately from empirical relations;¹ however, the following arguments show that attempts of this kind are a fruitless endeavor.

The reactions with which we are mostly concerned in chemistry take place in solution rather than in the gas phase. The majority of them moreover involve reactants, products, or transition states carrying electric charges. In such cases the entropies of solvation are extremely large, and these entropies cannot be estimated at present. This immediately rules out any possibility of estimating absolute values of equilibrium or rate constants for reactions of this kind. If we are concerned with absolute calculations of rates and equilibria, we must confine ourselves either to gas-phase reactions, or to reactions of non-polar type. Even here we will usually be forced to make estimates of entropies that are of dubious significance; chemical theory has not yet progressed to a point where problems of this kind can usefully be discussed.

Since chemical reactions involve only relatively minor changes in the reactants, the number of basic types of reaction is quite limited. One major problem in chemistry is the way in which the rate or equilibrium constant of a given type of reaction varies with the structures of the reactants. This is a much simpler problem than the one discussed above for it is concerned not with

the *absolute* values of equilibrium and rate constants but with their *relative* values for a set of similar reactions. Thus if k_0 is the rate constant for one particular reaction of a set, the quantity we need to know for some other reaction is not the rate constant k itself, but the ratio k/k_0 . From Eqs. (2) and (3),

$$-RT \log k/k_0 = (\Delta H_0^\ddagger - \Delta H^\ddagger) - T(\Delta S_0^\ddagger - \Delta S^\ddagger) \quad (4)$$

If now we are prepared to assume that for such a pair of closely related reactions,

$$\Delta S_0^\ddagger = \Delta S^\ddagger \quad (5)$$

then

$$-RT \log k/k_0 = \Delta H_0^\ddagger - \Delta H^\ddagger \quad (6)$$

It can be shown that if Eq. (5) holds, then

$$\Delta H_0^\ddagger - \Delta H^\ddagger = \Delta E_0^\ddagger - \Delta E^\ddagger \quad (7)$$

where ΔE_0^\ddagger , ΔE are the differences in internal energy between the reactants and the transition state; hence,

$$-RT \log k/k_0 = \Delta E_0^\ddagger - \Delta E^\ddagger \quad (8)$$

For a reversible reaction the same assumptions lead to the equivalent relations:

$$-RT \log K_0 = \Delta E_0 - \Delta E \quad (9)$$

The present theory of chemical reactivity rests on the use of Eqs. (8) and (9) and hence implicitly on the assumption of Eq. (5).

This assumption is not only unjustifiable in theory, but unjustified in practice. As Hammett² emphasized twenty years ago, the entropies of reaction or activation are not usually the same for a series of reactions of similar type. A good example is provided by the dissociation of carboxylic acids in water:



The entropies of ionization vary over a wide range with changes in R. Nevertheless current chemical theory has been very successful in relating the strengths of such acids to chemical structure. How can we account for this apparent anomaly?

The main contributions to ΔS or ΔS^\ddagger for polar reactions in solution come from the entropies of solvation. If there is an increase in solvation during a reaction, then ΔS will be negative. If this increase is different for different individual reactions of a series, then ΔS will likewise differ. However, the increase in solvation during the reaction will lead to a decrease in energy, i.e. ΔH will decrease. Since ΔH and ΔS appear with opposite signs in ΔF (Eq. (3)), the net effect on ΔF , and so on the equilibrium constant K , may be small. If then we calculate the relative equilibrium constants for the reactions using Eq. (9), i.e. with the assumption that all the reactions are following a common course with the same value for ΔS , our estimates of the ratios K/K_0 may be quite good. The same argument applies of course to calculations of relative rate constants using Eq. (8). A more detailed discussion of this will be found in a paper by Dewar and Sampson.³

Although this argument explains why current chemical theory is successful, and although it justifies the use of Eqs. (8) and (9) and so opens up chemical reactivity to study by existing quantum mechanical methods, it does so only with qualifications.

In the first place the cancellation of the effects of changes in ΔH and ΔS clearly cannot be expected to be exact; we cannot therefore hope to calculate even relative reactivities exactly. The most we can hope for is a general correspondence between the reactivities we calculate and those we observe.

Secondly, we must not try to compare our calculated values for ΔE or ΔE^\ddagger with observed heats of reaction or activation; this would clearly be gross error for reactions where the ΔS or ΔS^\ddagger differ in view of the compensating changes in ΔH or ΔH^\ddagger . It is therefore usually a waste of time to measure heats and entropies of reaction for polar reactions in solution since it is usually impossible to provide any reliable interpretation of them. The rates of reaction are the things that matter.

Thirdly, the compensation of ΔS and ΔH does not extend to situations where steric effects are important. Steric effects limit the configurations of the molecules concerned and so decrease the entropy of the system, but they also *increase* the energy. Here the changes in H and S synergize each other. Thus a reaction leading to an increased steric constraint will appear to have an

abnormally high value for ΔF or ΔF^\ddagger and so take place unexpectedly slowly. It is usually impossible to estimate these changes quantitatively with any assurance, but we must at least allow qualitatively for their effects on equilibrium or rate constants. This, of course, is the usual practice in chemistry; we estimate what would happen if there were no steric constraints, and then attribute the differences between what we estimate and what we observe to steric hindrance.

II. CHEMISTRY AS AN EXERCISE IN PERTURBATION THEORY

Let us consider first the simpler case of a reversible reaction; here we need to estimate the difference in total energy between the reactants and the products. We could of course do this indirectly, by calculating the total energies of each and finding ΔE by difference. However, the total energies are very large and the difference ΔE relatively small; it is clear that small errors in estimating the total energies may have a disastrous effect on ΔE .

Now as we have already remarked, the reactants and products of a chemical reaction usually differ but little. This difference can be represented by writing the Hamiltonian, H_P , of the products in the form:

$$H_P = H_R + P \quad (11)$$

where H_R is the Hamiltonian for the reactants and P a relatively small perturbation. The difference in energy between reactants and products, i.e. ΔE , now appears as a difference in energy between an unperturbed system, represented by H_R , and a perturbed system, represented by H_P . We can then estimate ΔE directly by using perturbation theory. This approach is particularly effective since P is known to be small; moreover the calculation of ΔE by perturbation theory is often much simpler than the calculation of total binding energies.

The same arguments apply with even greater force to rates of reactions. The calculation of rate constants is a much more difficult problem than the calculation of equilibria because we cannot determine the structures of transition states experimentally. We should in principle calculate the whole potential energy

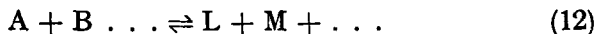
surface for the reaction and use this to estimate both ΔE^\ddagger and the structure of the transition state. Although this cannot be done at present for any but the simplest reactions (e.g., $D + H_2 \rightarrow DH + H$), we can often use perturbation theory directly to distinguish between possible structures for transition states.

Chemistry can in short be regarded as a classical exercise in perturbation theory.

III. DELOCALIZATION ENERGY AS THE DETERMINING FACTOR

In the present state of quantum chemistry, it is impossible to treat large molecules except in a most primitive way. One is usually forced to accept the localized bond approximation, treating σ bonds and unconjugated π bonds as being formed by the localized sharing of pairs of electrons between pairs of atoms. This approximation will be discussed in more detail below (Section XII); for many purposes it is found in practice to be quite satisfactory. The energy of a molecule is then written as a sum of the energies of inner-shell and lone-pair electrons localized on individual atoms, of electrons localized in two-center bonds, and of electrons which are delocalized over three or more nuclei. The delocalized electrons are those occupying the π MO's of conjugated systems, three-center MO's of the kind appearing in π complexes or boron hydrides, and analogous structures in transition states. Orbitals of this kind cannot be transformed into localized two-center orbitals; in conventional terminology molecules containing such structures must be written as resonance hybrids of two or more classical structures containing only localized bonds.

Consider a reversible reaction



The total energy (E_R) of the reactants can be written:

$$E_R = \sum_i^R E_i + \sum_{i,j}^R E_{ij} + E_D^R \quad (13)$$

where E_i is the energy of the electrons localized on atom i , E_{ij} the energy of electrons forming localized bonds between atoms i, j , and E_D the energy of delocalized electrons. The superscript R shows that the terms refer to the reactants (A, B, . . .). Likewise the energy (E_P) of the products can be written:

$$E_P = \sum_i^P E_i + \sum_{i,j}^P E_{ij} + E_D^P \quad (14)$$

The energy change (ΔE) in the reaction is then—

$$\Delta E = \left(\sum_i^P E_i - \sum_i^R E_i \right) + \left(\sum_{i,j}^P E_{ij} - \sum_{i,j}^R E_{ij} \right) + (E_D^P - E_D^R) \quad (15)$$

Now if we are comparing the equilibrium constants for a series of similar reactions, in which the bonds being formed or broken are the same in each case, it is easily seen that the terms in the first two pairs of parentheses in Eq. (15) will be the same for each reaction. We can then write ΔE in the form:

$$\Delta E = \Delta E_L + \delta E_D \quad (16)$$

where ΔE_L is the value that ΔE would have if the reactants and products contained only localized bonds. Now if we suppose that the entropy change is the same in each reaction, the equilibrium constant K is given (cf. Eqs. (4) and (7)) by:

$$-RT \log K = C + \Delta E \quad (17)$$

where C is a constant. The value of K relative to that (K_0) for one standard reaction of the series is then given by:

$$\begin{aligned} -RT \log (K/K_0) &= \Delta E - \Delta E_0 \\ &= \delta E_D - (\delta E_D)_0 \end{aligned} \quad (18)$$

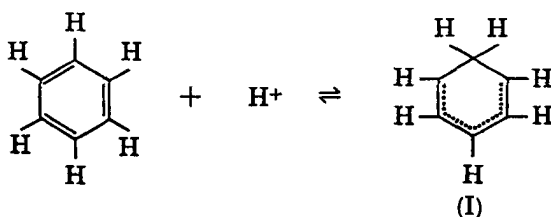
The relative values of the K 's are therefore determined only by the relative values of δE_D , the differences in delocalization energy between reactants and products or *delocalization energies of reaction*.

A similar argument shows that if we are comparing the rate constants for a series of irreversible reactions, these will follow the relation

$$-RT \log (k/k_0) = \delta E_b^\ddagger - (\delta E_b^\ddagger)_0 \quad (19)$$

where δE_b^\ddagger is the difference in delocalization energy between the reactants and the transition state, i.e. the *delocalization energy of activation*.

Thus if we are interested only in the relative values of equilibrium or rate constants for closely similar reactions, we need only concern ourselves with changes in delocalization energy. This of course is a useful simplification. A good illustration is provided by the protonation of aromatic hydrocarbons. Aromatic hydrocarbons react with strong acids to form salts. These are now known⁴ to be arenonium ions; thus benzene is converted to benzenonium ion (I) by strong acids:



The total bond energy (E_B) of benzene may be written:

$$E_B = 6E_{\text{CH}} + 6E_{\text{CC}} + E_{\pi} \quad (20)$$

where $E(1s)$ is the bond energy of a carbon $1s$ electron, E_{CH} and E_{CC} are the bond energies of the CH and CC σ bonds, and E_{π} is the energy of the delocalized (π) electrons. The total energy (E_{BH^+}) of (I) may likewise be written:

$$E_{\text{BH}^+} = 5E_{\text{CH}} + 2E'_{\text{CH}} + 4E''_{\text{CC}} + 2E'_{\text{CC}} + E'_{\pi} \quad (21)$$

Here E'_{CC} is the bond energy of a CC σ bond linking methine groups, E''_{CC} that of a CC σ bond adjacent to methylene, and E'_{CH} that of a methylene CH bond. The bond energies E'_{CC} , E'_{CH} differ from E_{CC} , E_{CH} since the carbon atoms are in a different state of hybridization.⁵ The bond energies E_{CC} , E'_{CC} will differ if the bonds linking the methine groups in I differ in length from those in benzene. The energy of reaction (ΔE_0) then becomes:

$$\Delta E_0 = 4(E'_{\text{CC}} - E_{\text{CC}}) + 2(E''_{\text{CC}} - E_{\text{CC}}) + 2(E'_{\text{CH}} - E_{\text{CH}}) + (E'_{\pi} - E_{\pi}) \quad (22)$$

Now the bond lengths of the CC bonds in aromatic compounds vary over only a small range; it is reasonable to suppose that the bond energies of their σ components will all be much the same. This should also be true of the bonds in arenonium ions such as I.

If we assume that the bond energies of all such σ bonds are in fact identical, then

$$\Delta E_0 = \delta E_0 + (\delta E_\pi)_0 \quad (23)$$

where δE_0 is the change in bond energy of σ bonds formed by the carbon atom at which protonation takes place, and $(\delta E_\pi)_0$ is the π energy of reaction.

Now consider protonation of some other hydrocarbon. Making the same assumptions and approximations as before, it is easily seen that the energy of reaction (ΔE) is given by:

$$\Delta E = \delta E_0 + \delta E_\pi \quad (24)$$

where δE_0 has the same value as before. If we are also prepared to assume that the change in solvation energy during protonation is the same for different hydrocarbons, the equilibrium constants K for the reaction



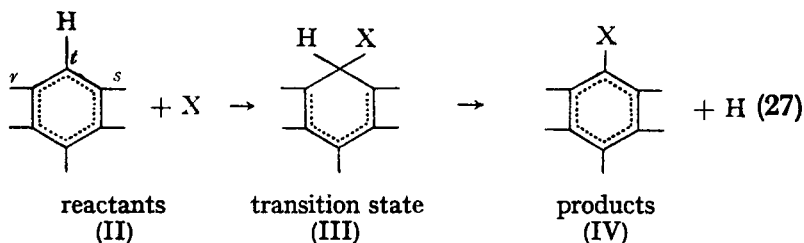
will obey the relation

$$-RT \log K/K_0 = \delta E_\pi - (\delta E_\pi)_0 \quad (26)$$

where K_0 , $(\delta E_\pi)_0$ are the values appropriate for benzene. The relative basicities of the hydrocarbons are then determined solely by their relative π energies of reaction.

IV. AROMATIC SUBSTITUTION; ~~FREE~~ VALENCE

The arguments given above may be best illustrated by an example: the rates of substitution reactions in simple aromatic systems. We shall assume first that the transition states are arenonium ions or radicals, i.e.



This picture of the transition state was first introduced by Wheland.⁶ Accepting it, and using the arguments and approximations of the last section, we see at once that the activation energy ΔE^\ddagger will be given by

$$\Delta E^\ddagger = \delta E_\sigma^\ddagger + \delta E_\pi^\ddagger \quad (28)$$

where δE_σ^\ddagger is the difference in total bond energy of σ bonds formed by the carbon atom at which reaction occurs between the reactants and the transition state, and δE_π^\ddagger is the corresponding difference in π energy.

If we are concerned only with relative rates of reaction, the rate constants will be given by

$$-RT \log (k/k_0) = \delta E_\pi^\ddagger - (\delta E_\pi^\ddagger)_0 \quad (29)$$

where k_0 , $(\delta E_\pi^\ddagger)_0$ refer to substitution in some standard compound (e.g., benzene). Our problem then is to determine the π energies of activation, δE_π^\ddagger .

These π energies could be found by calculating the total π energies of the aromatic compound and of the transition state and finding δE_π^\ddagger by difference; many calculations of this kind have been reported⁷ and some specific examples will be considered below (Section XIII). Since, however, this difference is only a small fraction of the total π energy, it should be possible to find it directly by using perturbation theory. This is the approach we shall consider in this section.

If we neglect differential overlap, the total π energy of a conjugated system may be written:

$$E_\pi = \sum_i q_i \alpha_i + 2 \sum_{i < j} p_{ij} \beta_{ij} \quad (30)$$

where q_i is the π -electron density at atom i and p_{ij} is the bond order of the bond between atoms i, j . The quantities α_i , β_{ij} are treated as empirical constants in the Hückel method, being described as coulomb and resonance integrals respectively. In the Pople SCF treatment⁸ they are given by:

$$\alpha_i = W_i + \frac{1}{2} q_i(ii, ii) + \sum_{j \neq i} \{ (q_i - 1)(ii, jj) + (ii, j) \} \quad (31)$$

$$\beta_{ij} = (\beta_{ij})_0 + \frac{1}{2} p_{ij}(ii, jj) \quad (32)$$

Here W_i is the ionization potential of an electron in the p -AO of an isolated atom i , $(\beta_{ii})_0$ is the one-electron exchange integral between the AO's of atoms i, j , and (ii, jj) and (ii, j) are the usual electron repulsion and penetration integrals. In practice the penetration integrals are usually disregarded; this should certainly be justifiable in the present connection where we are concerned only with differences in energy between closely related systems. Equation (31) then becomes—

$$\alpha_i = W_i + \frac{1}{2}q_i(ii, ii) + \sum_{j \neq i} (q_j - 1)(ii, jj) \quad (33)$$

Let us first consider substitution in an even alternant⁹ hydrocarbon (AH), i.e. one where the conjugated atoms are even in number and can be divided into two classes such that no two atoms of the same class are directly linked. It can be shown that the charge densities q_i at each position in such a hydrocarbon are all unity, both in the Hückel treatment⁹ and also in the Pople SCF approximation.¹⁰ Consider, first, substitution by a free radical; here the transition state will be an odd AH radical, the π -electron system of which contains one atom less than that of the original hydrocarbon. Let the atom at which substitution occurs be atom t , and the adjacent atoms be atoms r, s (Eq. (27)). Since the transition state is an odd alternant radical, the π -electron charge densities at each atom in it will also be unity.^{9,10} The conversion of the hydrocarbon to the transition state can thus be regarded as a perturbation in which the resonance integrals of the π bond between atom t and its neighbors decrease to zero. Now a change $\delta\beta_{it}$ in the resonance integral of one bond in an even AH leads to a change (δE_π) in the total π energy, given (cf. Eq. (30)) by:

$$\begin{aligned} \delta E_\pi &= \frac{\partial E_\pi}{\partial \beta_{it}} \delta\beta_{it} + O(\delta\beta_{it})^2 \\ &= 2p_{it}\delta\beta_{it} + O(\delta\beta_{it})^2 \end{aligned} \quad (34)$$

Our perturbation consists of a change in two resonance integrals from their initial value β_{rt}, β_{st} to zero. Neglecting second order terms, the required π -energy difference in Eq. (29) is given by:

$$\delta E_\pi^\ddagger = -2p_{rt}\beta_{rt} - 2p_{st}\beta_{st} \quad (35)$$

Since the bonds in aromatic hydrocarbons are similar in length and so must also have similar resonance integrals, we may reasonably suppose that all such integrals have a common value, β . In this case

$$\delta E_{\pi}^{\ddagger} = -2\beta(p_{rt} + p_{st}) \quad (36)$$

Now it can be shown¹¹ that the sum of the bond orders of the π bonds formed by a given carbon cannot have a value greater than $\sqrt{3}$; if the sum of the π bond orders has some lower value, this suggests intuitively that the carbon atom is not making full use of its potential ability to form π bonds. It has been suggested¹² that this difference, which has been termed the *free valence number* of the atom concerned, should be a measure of the ease with which chemical attack should take place at that atom, an idea clearly analogous to Thiele's theory of partial valence. The free valence number (f_t) of atom t in our AH is given by:

$$f_t = \sqrt{3} - p_{rt} - p_{st} \quad (37)$$

Combining this with Eq. (36),

$$\delta E_{\pi}^{\ddagger} = 2\beta(f_t - \sqrt{3}) \quad (38)$$

Equation (29) now becomes:

$$-RT \log (k/k_0) = 2\beta(f_t - (f_t)_0) \quad (39)$$

Since β is negative, k should be greater, the greater f_t ; this of course agrees with the intuition indicated above.

Now let us consider electrophilic substitution. Here the transition state will be in odd AH cation, derived from the corresponding radical by loss of one electron. In addition to disconnecting electron t from the π system, we now also have to change the charge densities of the remaining atoms by amounts δq_i . The corresponding changes in δE_{π} can again be found by a Taylor expansion from Eq. (30); taking only first-order terms,

$$\begin{aligned} \delta E_{\pi} &= \sum_i \frac{\partial E_{\pi}}{\partial q_i} \delta q_i = \sum \alpha_i \delta q_i \\ &= \alpha \sum \delta q_i = -\alpha \end{aligned} \quad (40)$$

The last two steps follow since α_i has the same value (α) at each position in an even AH (cf. Eq. (33) with $q_i = q_j = 1$), and since the sum of the δq_i is equal to -1 , being the change in total charge on the conjugated system in going from the radical to the carbon. The π energy of activation is then given by:

$$\delta E_{\pi}^{\ddagger} = -\alpha - 2\beta(p_{ri} + p_{si}) \quad (41)$$

Equation (39) therefore remains unchanged since the term in α cancels. An exactly similar argument holds for nucleophilic substitution; we therefore conclude that (1) the relative reactivities of different hydrocarbons, and the relative reactivities of different positions in the same hydrocarbon, should be the same for substitution by reagents of all kinds, and (2) there should be in each case a linear relation between $\log k$ and f_i .

The first relationship holds qualitatively in all cases except where steric effects are involved; thus naphthalene is more reactive than benzene to reagents of all three types (e.g. nitric acid, phenyl radicals, sodamide), and in each case the α -position in naphthalene is more reactive than the β ; the corresponding free valence numbers are:

naphthalene - α	0.453	
naphthalene - β	0.404	(42)
benzene	0.399	

The second relation also holds in the few cases where data are available; for examples and references see ref. 7 and a recent monograph by Streitwieser.¹³

The free valence number therefore provides a good guide to reactivity in alternant hydrocarbons; unfortunately this approach cannot easily be extended to compounds of other types. It can be used only when the contribution to $\delta E_{\pi}^{\ddagger}$ due to changes in the q_i is the same for different aromatic systems and this is so only if coulomb integrals α_i are the same for all the atoms present. Equation (33) shows that this is not so for molecules containing heteroatoms; the ionization potential W_i is different for different atoms. Equation (33) shows that non-alternant hydrocarbons such as azulene must also be excluded; here the

π -electron densities q_i are no longer unity so the contributions of the terms involving them differ from atom to atom.

These difficulties will of course be greater in the case of electrophilic or nucleophilic substitution, but they will appear also in the case of substitution by radicals. The π -electron charge densities q_i in the transition state will no longer be the same as in the reactant if heteroatoms are present, if the compounds are non-alternant; these changes will lead to corresponding changes in δE_π^\ddagger which are not included in the treatment given above.

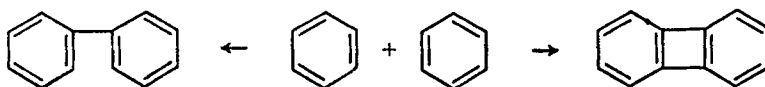
These points need emphasizing, for the use of free valence as a measure of reactivity was first introduced on intuitive grounds, based on the Thiele theory of partial valence. On this basis there seems no obvious reason why free valence should serve as a measure of reactivity only for compounds of one type. The perturbational treatment given above shows that the validity of the correlation is due merely to a fortuitous coincidence which holds only for alternant hydrocarbons.

V. THE PMO METHOD

The approach used in the previous section involved the use of perturbation theory in the LCAO MO approximation. This treatment, which has been termed the perturbational MO (PMO) method,¹⁴ can be used very generally in discussing chemical problems, and a general treatment of the structure and reactivity of organic compounds in such terms was given some time ago.¹⁴ Here we will introduce a simpler and more powerful perturbational procedure for calculating energy differences of the kind discussed in the previous section. Problems of this kind involve comparisons of π energy of pairs of systems differing only in that one member has an additional conjugated atom. In the previous section we did this by treating the united system as the unperturbed system, the perturbation being the excision of one carbon atom from conjugation with the rest. Here we follow the reverse procedure of treating the lesser system as the unperturbed one, the perturbation now consisting of the addition of an extra atom.

This is a special case of a general problem: given two isolated conjugated systems R , S , what will be the change in π energy when they are united? By union we mean the linkage of one or

more atoms of R to corresponding atoms in S by σ bonds across which the two conjugated systems can interact; thus union of two molecules of benzene could give biphenyl or biphenylene:



The case in which we are interested is the special one where one of the "conjugated" systems is a simple methyl group; here the " π -electron system" consists of a single carbon $2p$ -AO.

In this section we will give a solution¹² in terms of the Hückel approximation; the differences introduced by using SCF methods will be discussed later (Section XIV). We will write the MO's of R as Φ_m , of S as Ψ_n , given in terms of the respective AO's φ_i , ψ_k , by:

$$\begin{aligned}\Phi_m &= \sum_i a_{mi} \varphi_i & (\text{energy } E_m) \\ \Psi_n &= \sum_k b_{nk} \psi_k & (\text{energy } F_n)\end{aligned}\tag{43}$$

The energies of the MO'S (E_m , F_n) are reckoned relative to that of a carbon $2p$ -AO. We assume first that R , S are even AH's; in this case the MO's appear in pairs⁹ given by:

$$\begin{aligned}\Phi_m^+ &= \sum_i^* a_{mi} \varphi_i + \sum_j^{\circ} a_{mj} \varphi_j & (\text{energy } E_m) \\ \Phi_m^- &= \sum_i^* a_{mi} \varphi_i - \sum_j^{\circ} a_{mj} \varphi_j & (\text{energy } -E_m)\end{aligned}\tag{44}$$

with similar expression for the MO's of S . Here the symbols \sum_i^* , \sum_j° imply summation over one or other of the two sets (starred or unstarred) into which the conjugated atoms can be divided, no two atoms of the same set being directly linked.

We assume the union of R to S in RS to be through atom r in R atom s in S . The perturbation involved in uniting R to S leads to an increase in the resonance integral of the bond between atoms r , s from zero to β_{rs} (its value in RS). The perturbation P

is then defined in terms of the basis set of AO's φ_i , ψ_k by the matrix elements:

$$\begin{aligned}\int \varphi_i \mathbf{P} \varphi_j d\tau &= \int \psi_k \mathbf{P} \psi_l d\tau = 0 \\ \int \varphi_i \mathbf{P} \psi_k d\tau &= 0, \quad \text{unless } i = r, k = s \\ \int \varphi_r \mathbf{P} \psi_s d\tau &= \beta_{rs}\end{aligned}\quad (45)$$

Consider the unperturbed MO Φ_m of energy E_m . If there is no degeneracy, the first order perturbation (δE_m^I) due to union of R and S is given by—

$$\delta E_m^I = \int \Phi_m \mathbf{P} \Phi_m d\tau = \sum_i \sum_j a_{mi} a_{mj} \int \varphi_i \mathbf{P} \varphi_j d\tau = 0 \quad (46)$$

This result still holds if there is degeneracy between two or more orbitals of R . Under these conditions there is no first order perturbation to the MO's of R ; a similar argument shows that those of S likewise remain unchanged. This of course is because the perturbation involves a region (between atoms r, s) not covered by the unperturbed MO's.

The second order perturbation, δE_m^{II} , can be found at once:

$$\begin{aligned}\delta E_m^{II} &= \sum_n \frac{(\int \Phi_m \mathbf{P} \Psi_n d\tau)^2}{E_m - F_n} = \sum_n \frac{[\sum_i \sum_k a_{mi} b_{nk} \int \varphi_i \mathbf{P} \psi_k d\tau]^2}{E_m - F_n} \\ &= \sum_n \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n}\end{aligned}\quad (47)$$

Likewise the second order perturbation to the level F_n is given by:

$$\delta F_n^{II} = \sum_m \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{F_n - E_m} \quad (48)$$

The total change (δE) in π energy in uniting R to S is then given, to a second approximation, by

$$\delta E = \sum_m n_m \sum_n \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} + \sum_n n_n \sum_m \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{F_n - E_m} \quad (49)$$

where n_m is the number of electrons in the MO Φ_m , n_n that in Ψ_n . Since R and S are even AH's in which all the MO's are either doubly occupied or empty, we write this in the form:

$$\begin{aligned}\delta E &= 2 \sum_m^{\text{occ}} \sum_n^{\text{all}} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} + \sum_m^{\text{all}} \sum_n^{\text{occ}} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{F_n - E_m} \\ &= 2 \left[\sum_m^{\text{occ}} \sum_n^{\text{unocc}} - \sum_m^{\text{unocc}} \sum_n^{\text{occ}} \right] \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n}\end{aligned}\quad (50)$$

where the superscripts occ, unocc, all refer to summation over occupied MO's, unoccupied MO's or all the MO's of a given set. It is at once evident from Eq. (44) that the denominator of Eq. (50) is negative, for all the occupied MO's have negative energies, all the unoccupied ones positive energies. The union of R to S therefore leads to a decrease in energy. It is also obvious that this decrease is small, for the denominator of each term is large, being the difference in energy between a bonding MO of R and an antibonding MO of S , or conversely. The mutual interaction of the filled bonding MO's leads to no change in total energy. Since R, S are AH's, we may use Eq. (44) to simplify this expansion still further:

$$\delta E = 4 \sum_m^{\text{occ}} \sum_n^{\text{occ}} \frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m + F_n} \quad (51)$$

Since the sums $(E_m + F_n)$ are larger than the variations in E_m or F_n , we may without serious error replace E_m, F_n by mean values \bar{E}_m, \bar{F}_n ; these will moreover be much the same for different AH's. Writing their sum as ΔE ,

$$\delta E = \frac{\beta_{rs}^2}{\Delta E} \sum_m^{\text{occ}} 2a_{mr}^2 \sum_n^{\text{occ}} 2b_{ns}^2 = \frac{\beta_{rs}^2}{\Delta E} q_r q_s = \frac{\beta_{rs}^2}{\Delta E} \quad (52)$$

The second order effect of uniting R to S is therefore not only small, but also much the same for different pairs of hydrocarbons R, S . If we estimate bond energies empirically, the major part of this perturbation energy will be tacitly included in our value for the bond energy of a single bond between sp^3 carbon atoms; in a series of similar reactions, contributions of this kind will be

the same throughout and so will have no effect on the relative rates of equilibria.

The situation is different if there is degeneracy between a MO (Φ_m) of R and one (Ψ_n) of S . In this case there is a first order perturbation δE given by the secular equation;

$$\begin{vmatrix} (\int \Phi_m \mathbf{P} \Psi_m d\tau - \delta E) & \int \Phi_m \mathbf{P} \Psi_n d\tau \\ \int \Phi_n \mathbf{P} \Psi_m d\tau & (\int \Psi_n \mathbf{P} \Psi_n d\tau - \delta E) \end{vmatrix} = 0 \quad (53)$$

Substituting from Eqs. (43) and (45) as before, we find:

$$\begin{vmatrix} -\delta E & a_{mr} b_{ns} \beta_{rs} \\ a_{mr} b_{ns} \beta_{rs} & -\delta E \end{vmatrix} = 0 \quad (54)$$

whence

$$\delta E = \pm a_{mr} b_{ns} \beta_{rs} \quad (55)$$

The corresponding perturbed MO's are:

$$\frac{1}{\sqrt{2}} (\Phi_m + \Psi_n); \quad \frac{1}{\sqrt{2}} (\Phi_m - \Psi_n) \quad (56)$$

If the MO's of R , S were both filled, there would still be no net change in energy, for the perturbations are equal and opposite for the two pairs of electrons occupying them. If R and S are AH's, all bonding MO's must be full and all antibonding MO's empty. Consequently the only place where a first order perturbation can arise is when R , S are both odd AH's. In an odd AH there is necessarily one MO left over for the pairing scheme of Eq. (44); this *non-bonding MO* (NBMO)^{9,15} has zero energy and is composed of one set of atoms only, which we take to be the starred set. The NBMO's of R , S are then:

$$\Phi_0 = \sum_i a_{0i} \varphi_i; \quad \Psi_0 = \sum_k b_{0k} \psi_k \quad (\text{energy} = 0) \quad (57)$$

If R , S are odd AH radicals, with singly occupied NBMO's, there will then be a first order change in energy when they are united to RS , given by:

$$\delta E = 2a_{0r} b_{0s} \beta_{rs} \quad (58)$$

The energy relations are indicated in Fig. 1.

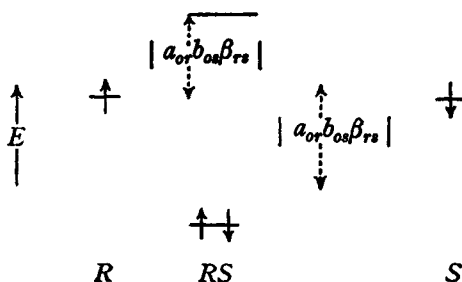


Fig. 1. NBMO's of R , S and of the corresponding MO's of RS .

The coefficients a_{or} , b_{os} can be found by an extremely simple procedure pointed out first by Longuet-Higgins;¹⁵ it takes only a few seconds to calculate the coefficients for odd AH's containing as many as twenty or thirty atoms. Full details have been given so often¹³⁻¹⁶ that there is no need to repeat them here.

These results can at once be generalized to cases where R , S are united at more than one point, through atom r in R to atom s in S , through atom t in R to atom u in S , etc. In this case Eqs. (50) and (58) become:

$$\delta E = 4 \sum_m^{\text{occ}} \sum_n^{\text{occ}} \frac{[\sum_{i,j} a_{mi} b_{nj} \beta_{ij}]^2}{E_m - E_n} \quad (59)$$

$$\delta E = 2 \sum_{i,j} a_{oi} b_{oj} \beta_{ij} \quad (60)$$

The sums are over all pairs of atoms i , j through which R is united with S in RS .

Returning to the problem of aromatic substitution, we see that this is an example of the special case where R , S are odd AH's. Here R is the transition state, an odd AH, while S is methyl; methyl can be regarded as the limiting case of an odd AH whose "NBMO" is a single carbon $2p$ -AO. This of course has the same energy (zero on our scale) as a NBMO; the corresponding "coefficient" b_{os} will be unity. If the NBMO coefficients of atoms r , s in the transition state are a_{or} , a_{os} respectively,

$$\delta E_n^\ddagger = -2(a_{or}\beta_{rt} + a_{os}\beta_{st}) \quad (61)$$

(The *minus* sign appears because δE_{π}^{\dagger} is defined as the difference in energy between the even AH and the transition state derived from it by loss of atom t for the conjugated system). If we assume equal resonance integrals for aromatic bonds, this can be written:

$$\delta E_{\pi}^{\dagger} = -\beta N_t \quad (62)$$

where

$$N_t = 2(a_{or} + a_{os}) \quad (63)$$

Equation (29) becomes:

$$-RT \log (k/k_0) = -\beta(N_t - (N_t)_0) \quad (64)$$

Since β is negative, substitution should occur more readily the smaller the *reactivity number* N_t ; also there should be a linear relation between $\log k$ and N_t . Both these relations hold in practice.^{14,17}

The similarity between Eqs. (39) and (64) implies that there must be a relationship between free valence number and reactivity number. This is indeed the case, for it can be shown¹⁴ at once by first order perturbation theory that

$$P_{rt} = |a_{or}|; \quad P_{st} = |a_{os}| \quad (65)$$

Therefore as long as a_{or} and a_{os} have the same sign,

$$2\beta(f_t - (f_t)_0) = -\beta(N_t - (N_t)_0) \quad (66)$$

the coefficients a_{or} , a_{os} will have the same sign if, and only if atoms r , s , t form part of an open chain or of a $(4n + 2)$ -membered ring;¹⁸ this of course is the case in all alternant aromatic systems where substitution has been studied. The use of the free valence number as a measure of reactivity is therefore restricted not merely to AH's, but to AH's when substitution takes place in an open chain or $(4n + 2)$ -membered ring.

Statistical studies indicate¹⁸ that the reactivity number provides the best measure of reactivity in AH's at present available. This is surprising in view of the simplicity of the method. The "calculations" involved in it can be carried out by anyone in a matter of seconds using only pencil and paper.

VI. EXTENSION TO HETEROAROMATIC SYSTEMS

The method outlined in the last section can be applied to any reaction involving the conversion of an even AH to an odd AH with one conjugated atom less, or of an odd AH to an even AH with one conjugated atom more. The method can be extended to alternant systems containing heteroatoms by the following procedure, due to Coulson and Longuet-Higgins.¹⁹

For any alternant system there is a corresponding *isoconjugate* AH, two molecules being described as isoconjugate if they contain the same number of conjugated atoms in the same stereochemical arrangement, and also the same number of π electrons. Thus the following molecules and ions are isoconjugate with benzene:



To a first approximation, the π -electron distributions in two isoconjugate molecules are the same; the π -electron densities and bond orders will therefore be approximately the same in an alternant heteroatomic molecule as in the isoconjugate AH. The π energy (E_π) of the former can then be calculated in terms of that ($(E_\pi)_0$) of the AH from Eq. (30):

$$E_\pi = (E_\pi)_0 + \sum_i a_i \delta a_i + 2 \sum_{i < j} p_{ij} \delta \beta_{ij} \quad (67)$$

In the case of an AH, q_i can be found¹⁵ at once;

$$\begin{array}{ll} \text{even AH} & q_i = 1 \text{ at all positions} \\ \text{odd AH radical} & q_i = 1 \text{ at all positions} \\ \text{odd AH cation} & q_i = 1 - a_{oi}^2 \\ \text{odd AN anion} & q_i = 1 + a_{oi}^2 \end{array} \quad (68)$$

We can often neglect the terms in Eq. (67) involving the $\delta \beta_{ij}$, for the π bonds formed by elements in which we are mainly interested have comparable strengths. In that case—

$$E_\pi = (E_\pi)_0 + \sum_i \delta \alpha_i \quad (\text{even AH, odd AH radical}) \quad (69)$$

$$E_\pi = (E_\pi)_0 + \sum_i (1 - a_{oi}^2) \delta \alpha_i \quad (\text{odd AH cation}) \quad (70)$$

$$E_\pi = (E_\pi)_0 + \sum_i (1 + a_{oi}^2) \delta \alpha_i \quad (\text{odd AH anion}) \quad (71)$$

Suppose we know the π activation energy, $(\delta E_{\pi}^{\ddagger})_0$, for a given reaction of an AH. We can then calculate $\delta E_{\pi}^{\ddagger}$, the activation energy for the corresponding reaction of the heteroatomic system, by using Eqs. (69)–(71). Consider for example substitution in an even heteroatomic molecule such as quinoline. The difference in π energy between the hydrocarbon and its transition state is given by:

$$(\delta E_{\pi}^{\ddagger})_0 = -\beta N_i \quad (72)$$

The difference in π energy between the isoconjugate heteroatomic molecule and the hydrocarbon is given by:

$$E_{\pi} - (E_{\pi})_0 = \sum_i \delta \alpha_i \quad (73)$$

The difference in π energy between the heteroatomic transition state and the hydrocarbon transition state is given by

$$E'_{\pi} - (E'_{\pi})_0 = \sum_i \delta \alpha_i \quad (\text{radical substitution}) \quad (74)$$

$$E'_{\pi} - (E'_{\pi})_0 = \sum_i (1 - a_{oi}^2) \delta \alpha_i \quad (\text{electrophilic substitution}) \quad (75)$$

$$E'_{\pi} - (E'_{\pi})_0 = \sum_i (1 + a_{oi}^2) \delta \alpha_i \quad (\text{nucleophilic substitution}) \quad (76)$$

Combining these results we find for the three types of reagents the following values for the π energy of activation for the heteroaromatic compound:

$$\text{radical substitution:} \quad \delta E_{\pi}^{\ddagger} = -\beta N_i \quad (77)$$

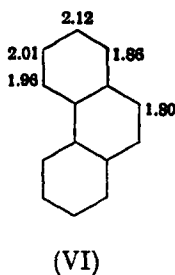
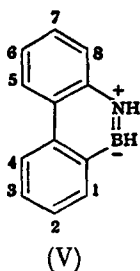
$$\text{electrophilic substitution:} \quad \delta E_{\pi}^{\ddagger} = -\beta N_i - \sum_i a_{oi}^2 \delta \alpha_i \quad (78)$$

$$\text{nucleophilic substitution:} \quad \delta E_{\pi}^{\ddagger} = -\beta N_i + \sum_i a_{oi}^2 \delta \alpha_i \quad (79)$$

Radical substitution should therefore take place about equally easily in the heteroaromatic system and in the AH; this appears to be the case.²⁰ Nucleophilic substitution should take place more easily in heteroaromatic compounds containing atoms more electronegative than carbon (e.g., N), and most easily in positions where N_i is small and a_{oi}^2 large; the observed reactivities follow this pattern.¹⁴ Likewise electrophilic substitution should be hindered in such compounds and should take place preferentially

in positions where a_{oi}^2 is small. The available evidence can be very well interpreted²¹ in terms of Eq. (79). One also arrives at once at a qualitative rule, that heteroatoms such as nitrogen accelerate nucleophilic substitution, and retard electrophilic substitution, most strongly at a position of opposite type to their own, for it is easily shown that if substitution takes place at an unstarred atom in an AH, then the NBMO coefficients a_{oi} vanish at all unstarred positions in the transition state.

A nice example is provided by 10,9-borazarophenanthrene (V). The reactivity numbers for the isoconjugate AH, phenanthrene, are shown in (VI). The lowest numbers are in the 9,1- and 4-positions; but the 4-position is sterically hindered. Experiment²² showed that the order of reactivity (nitration in acetic anhydride) for the various positions in phenanthrene was $9 > 1 > 3 \gg 4, 2$. In I, the 9- and 10-positions are of course blocked. The nitrogen atom, being more electronegative than carbon, will deactivate positions 1, 3, 5, 7, while the boron, being less electronegative than carbon (i.e. $\delta\alpha$ is now *positive*), will activate positions 2, 4, 6, 8. Evidently positions 6 and 8 should be the most reactive, with, presumably, 8 more reactive than 6; experiment²³ confirmed this prediction which was made before the experimental results were available. Detailed calculations²³ also indicated that the third most reactive position in II should be the 2-position; this also turned out to be the case.



This simple approach thus provides a very satisfactory account of reactions of this kind; it can be used with some assurance to predict reactivity and orientation in molecules for which experimental evidence is not available.

An amusing application to a reaction of quite different type

was reported recently by Pettit.²⁴ Aromatic aldehydes and ketones of the type ArCOR , where ArH is an even alternant hydrocarbon, show appreciable basicity, and their $\text{p}K$'s vary over a considerable range. Here salt formation involves the equilibrium:



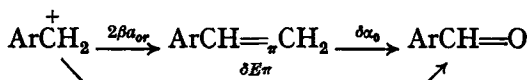
Since oxygen is very much more electronegative than carbon, it is reasonable to suppose that the ions approximate to the structure



In this case the basic dissociation constants K should follow the relation:

$$-RT \log (K/K_0) = (\delta E_\pi) - (\delta E_\pi)_0 \quad (82)$$

where δE_π is the difference in π energy between the aldehyde or ketone and the related arylmethyl carbonium ion, while $K_0, (\delta E_\pi)_0$ are the corresponding values for the case where Ar is phenyl. The quantity δE_π can be found from the cycle (cf. p. 92):



where $\delta\alpha_0$ is the difference in Coulomb integral between oxygen and carbon. It follows that

$$-RT \log (K/K_0) = 2\beta(a_{or} - (a_{or})_0) \quad (83)$$

This relation was found to hold quite accurately for a number of compounds of this type.

VII. THE TRANSITION STATE IN AROMATIC SUBSTITUTION

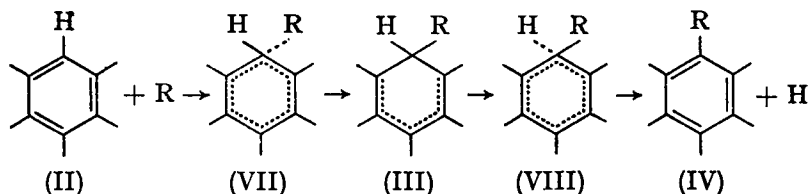
In the two previous sections it has been assumed that the transition state for aromatic substitution has the benzenonium structure (III); this leads to the prediction that a plot of $\log k$ against N_i (see Eq. (64)) should be a straight line of slope β/RT , regardless of the reagent used. Plots of this kind are linear for any one reaction, but the slopes are not the same for different reagents.

Moreover the values of β derived from them are much less than the values (20–30 kcal/mole) commonly used in Hückel calculations. Table I illustrates both these points.¹⁷ Clearly something is wrong; and this is most likely to be our model for the transition state.

TABLE I. Estimated Values for β for Various Substitution Reactions of AH's

Reaction	$-\beta$, kcal/mole
Nitration in Ac_2O	6.0
Chlorination in AcOH	11
Chlorination in AcOH/CCl_4	13
Methylation by CH_3	3.2
Trichloromethylation by CCl_3	6.0

There can be little doubt that the reactions pass at some stage through benzenonium structures (III); there is, however, no guarantee that these structures are transition states. It is entirely possible that the structures such as III are stable intermediates and that the transition states are intermediate either between the reactants and III, or between III and the product. We can write the corresponding reaction scheme:



The overall rate will still be given by:

$$-RT \log k = C + \delta E_{\pi}^{\ddagger} \quad (84)$$

However $\delta E_{\pi}^{\ddagger}$ now refers to the difference in π energy between the reactant II and a transition state or VIII in which the reaction center (carbon atom t) is still somewhat π -bonded to its neighbors (atoms r , s).

We can calculate $\delta E_{\pi}^{\ddagger}$ for this case by the same method as before, by relating the energy of VII (or VIII) to that of the benzenonium intermediate (III). The π bonds between atoms r , s and atom t are weak; this will correspond to their having a smaller resonance integral (β') than the usual value (β). The difference ($\delta E_{\pi}'$) in π energy between III and VII (or VIII) will then be given by

$$\delta E_{\pi}' = \beta' N_t \quad (85)$$

Using Eq. (62) we can now find the required π energy of activation;

$$\begin{aligned} \delta E_{\pi}^{\ddagger} &= -\beta N_t + \beta' N_t \\ &= -\beta'' N_t \end{aligned} \quad (86)$$

where

$$\beta'' = \beta - \beta' \quad (87)$$

Provided that all the reactions follow a similar reaction path, so that β' is the same in all the transition states, β'' will be constant. A plot of $\log k_t$ against N_t will then be linear, but its slope will be not β/RT , but β''/RT . The values for " β " in Table I are therefore really values of β'' . The fact that they vary, and are less than β , is thus explained—and also the fact that the $\log k_t/N_t$ plot is a straight line.

These conclusions have been confirmed experimentally,²⁵ for both electrophilic and nucleophilic substitution. There seems no doubt that structures such as III are stable entities rather than transition states. Moreover, as Melander and others have shown,²⁶ the absence of deuterium isotope effects in most electrophilic substitutions indicates that in such cases the transition state must be VII rather than VIII. The rate-determining step in the reaction is the formation of the intermediate (III).

The relationship between k_t and N_t can now be seen in a different light. It has long been known that in a series of closely related reactions, there is commonly a linear relation between heat of reaction and activation energy. If a change in the reactants alters the heat of reaction by δH , it will then alter the heat of activation by an amount $\epsilon \delta H$, where ϵ is a proportionality factor that is constant throughout the series of reactions. This relationship was explained some time ago by Evans, Polanyi and Bell²⁷ in terms of the crossing of potential energy surfaces.

It also follows from their arguments that the activation energy and proportionality factor ϵ should be less, the more exothermic the reaction, and that the transition state should be correspondingly closer in structure to the reactants. In our case it is clear that the partial bond to R in VII will be weaker, and the π bonds between atoms r, s and atom t will be stronger, the more exothermic the formation of III. This will correspond to a larger value of β' . Comparison of Eqs. (62) and (86) shows that the proportionality factor ϵ is here given by:

$$\epsilon = \beta''/\beta = 1 - \beta'/\beta \quad (88)$$

Thus the more exothermic and faster the reaction, the greater should be β' and the smaller β'' and ϵ .

A further corollary follows. Suppose we compare the relative reactivities of two carbon atoms u, v either in the same AH, or in different AH's to a variety of reagents. The relative rate constants are given in each case by:

$$-RT \log k_u/k_v = \beta''(N_v - N_u) \quad (89)$$

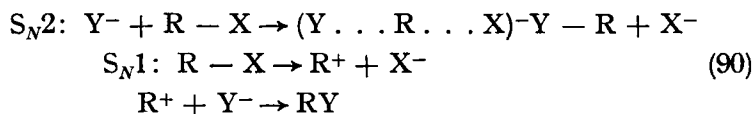
Thus the smaller β'' , the smaller will be the difference in rates. This is the basis of the "selectivity rule" proposed by Brown and Nelson;²⁸ the more reactive a given substituting agent, i.e. the more rapidly it attacks a given aromatic compound, the less selectivity it shows in choosing between one position and another.

VIII. DETERMINATION OF THE STRUCTURES OF TRANSITION STATES

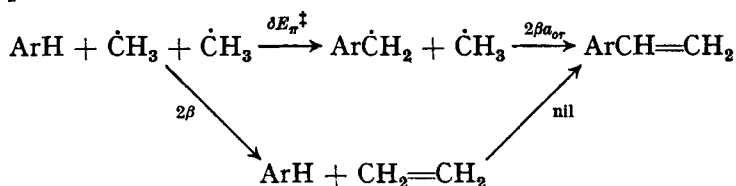
The previous sections have shown how simple quantum mechanical reasoning can be used to gain insight into a chemical reaction. The techniques used there should be applicable in many other cases. The essential point is that calculations can be carried out much more simply, and much more reliably, for hydrocarbons than for molecules containing heteroatoms. If we are concerned with the mechanism of a given reaction, we will then obtain most guidance from quantum theory if we can study the reactions of a wide range of hydrocarbons. So far surprisingly little use has

been made of this general principle; one further example will suffice to show its power.

Nucleophilic aliphatic substitution was believed some years ago to take place by two distant paths, one involving a one-step displacement, the other an intermediate carbonium ion. These two routes can be represented as follows, for the reaction between RX (R being an alkyl or substituted alkyl group) and a nucleophile Y^-



If this mechanism is correct for the S_N1 reaction, and if we can suppose that the transition state is an intimate ion pair R^+X^- , the energy of activation, for a series of alkyl derivatives RX , where R is varied, can be written in the form of Eq. (19). If R is an arylmethyl group $ArCH_2$, the term δE_D is then equal to the change in π energy in going from the original aryl system $ArCH_2X$ to the arylmethyl system where there is an additional conjugated carbon atom. This π -energy difference (δE_π^\ddagger) can be estimated^{14,20} by perturbation theory from the following cycle, the energies listed being first order changes in π energy at each step:



Here a_{or} is the NBMO coefficient of the AO of the methylene carbon in $ArCH_2$. We find:

$$\delta E_\pi^\ddagger = 2\beta(1 - a_{or}) \quad (92)$$

The rate constant for the reaction should then be given by:

$$\begin{aligned} -RT \log k &= C + \delta E_\pi^\ddagger \\ &= C' - 2\beta a_{or} \end{aligned} \quad (93)$$

where C , C' are constants for the reactions of compounds RX where only R is varied. A plot of $\log k$ against a_{or} should therefore be a straight line of slope $2\beta/RT$. This relation was found²⁹ to hold for the solvolysis of a number of arylmethyl chlorides in moist formic acid; the derived value of β was also reasonable (32 kcal/mole).

Equation (93) was derived for a pure or limiting S_N1 reaction, i.e. one involving a free carbonium ion intermediate. For such reactions the plot of $\log k$ against a_{or} should not only be linear, it should also have a constant slope. However, it turned out²⁹ that a similar linear relation was also obtained for the rates of the reactions of such chlorides with iodide ion in dry acetone:



These reactions are known to be of S_N2 type since they show second order kinetics. The value of β derived from the slope of the plot of $\log k$ vs. a_{or} was in this case very small (5 kcal/mole).

In the reactions with iodide ion there is strong participation by the nucleophile in the transition state. The transition state has the structure indicated in Fig. 2. Here the π -AO of the

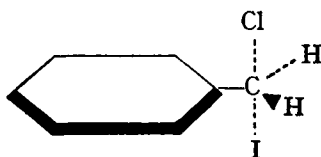
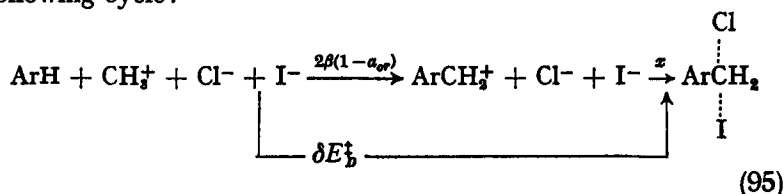


Fig. 2. Transition state for reaction of $ArCH_2Cl$ with I^- .

methylene carbon not only overlaps sideways with the p -AO of the adjacent atom in the ring, but also lengthways with AO's of Cl and I . The delocalized electrons are no longer π electrons since they also cover the nuclei of the Cl or I atoms.

In order to get an approximate estimate of δE_b^\ddagger , let us make the simplifying assumption that the electronegativities of all the atoms in the transition state are equal. (This can be shown to have no vital effect on the argument; introduction of differences in electronegativity by the perturbation methods outlined

earlier has no gross effect). We can now estimate δE_b^\ddagger by the following cycle:



In order to find the energy x , we use first order perturbation theory. The degenerate orbitals involved are the doubly occupied AO's of Cl^- and I^- , and the empty NBMO of ArCH_3 . The necessary matrix elements are found as before in terms of the CCl and Cl resonance integrals β_{Cl} , β_{I} . Solving the resulting three-row secular equation, we find for the perturbed energies—

$$+a_{or}(\beta_{\text{Cl}}^2 + \beta_{\text{I}}^2)^{\frac{1}{2}}; 0; -a_{or}(\beta_{\text{Cl}}^2 + \beta_{\text{I}}^2)^{\frac{1}{2}} \quad (96)$$

Two of the four electrons occupy the bonding orbital of the set, two the non-bonding orbital; hence:

$$x = -2a_{or}(\beta_{\text{Cl}}^2 + \beta_{\text{I}}^2)^{\frac{1}{2}} = 2a_{or}\beta' \quad (97)$$

where β' is a mean of β_{Cl} and β_{I} (the root mean square, taking the negative root since β_{Cl} and β_{I} are negative). Hence—

$$\begin{aligned} \delta E_b^\ddagger &= 2\beta(1 - a_{or}) + 2a_{or}\beta' \\ &= 2\beta - 2a_{or}(\beta - \beta') \end{aligned} \quad (98)$$

This leads to an expression for the rate constant:

$$-RT \log K = C - 2a_{or}(\beta - \beta') \quad (99)$$

This is of the same form as Eq. (93), accounting for the linear plot of $\log k$ vs. a_{or} ; however, the slope is no longer $2\beta/RT$, but $2(\beta - \beta')/RT$.

Now β' will be greater, the greater the covalent bonding between ArCH_3 and the departing group (Cl) and the entering nucleophile; the slope of the plot of $\log k$ against a_{or} should therefore provide a method for estimating the degree of nucleo-

philic participation in the transition state. Table II shows some examples of this.

TABLE II. Values of $\beta - \beta'$ for Various Reactions of Arylmethyl Chlorides

Reaction	$\beta - \beta'$, kcal
Solvolysis in 99.5% formic acid	32
Solvolysis in formic acid-dioxan-water	21
Solvolysis in 80% ethanol	9.5
Reaction with iodide ion in acetone	5

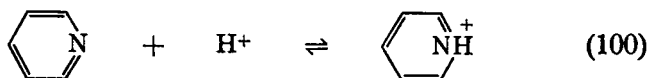
The order of decreasing $\beta - \beta'$ certainly follows the order expected, for water is a better nucleophile than formic acid, and better in neutral ethanol than in formic acid-dioxan, while iodide ion is better still. The interesting thing is that both the first two reactions are kinetically of S_N1 type, the rates being unaltered by addition of sodium formate, while the third reaction is of intermediate type, the rate varying with addition of alkali but not being first order in alkali concentration. Yet if our analysis is correct, the second and third reactions must both involve strong nucleophilic participation.

There has been much controversy in recent years concerning the relationship between the S_N1 and S_N2 reactions. Grunwald and Winstein³⁰ and Swain³¹ first suggested that the mechanisms of nucleophilic substitution might form a graded series in which participation by the nucleophile can cover a continuous range, rather than fall into two distinct categories with zero and large participation, and Doering and Zeiss³² and Doering and Streitwieser³³ have provided strong evidence for participation by the nucleophile in specific reactions of S_N1 type. The most definite evidence for these ideas has, however, been provided by the quantum chemical investigation outlined above; this has provided a method for studying quantitatively the extent of nucleophilic participation under different reaction conditions—and also a good illustration of the value of quantum theory in problems of this kind.

IX. ISOCONJUGATE REACTIONS AND SUBSTITUENT EFFECTS

In the reactions we have so far considered, the conjugated systems of the reactants and products (or transition states) have been different, and the different reactants of a series have also had different conjugated systems. In these cases one must calculate the corresponding changes in π energy, δE_π^\ddagger or δE_π , in order to obtain a valid criterion of reactivity. In many cases, however, the situation is simpler. Either the reactants and products (or transition state) are isoconjugate; or all the reactants of our series are isoconjugate and so also are all the products (or transition states). Reaction of one or other of these two classes may be termed *isoconjugate reactions*. Here the variations in δE_π or δE_π^\ddagger arise not from changes in the size or nature of the conjugated systems involved, but from changes in the electronegativity of constituent atoms or from changes in the electric potential due to the presence of polar or charged groups in the molecule. These ideas have been stated in terms of normal conjugated systems; they could of course be extended to more general types of delocalization.

A simple example of the first kind is provided by salt formation in heterocyclic bases; e.g.

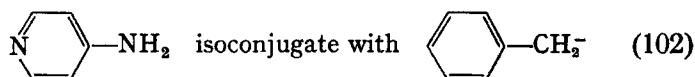


Here the product is isoconjugate with the base itself, the only difference being that the nitrogen atom has become more electronegative due to the attachment of a positively charged proton. So far as the delocalized (π) electrons are concerned, the only change is a decrease in the coulomb integral of nitrogen; to a first approximation the corresponding change in π energy will be given (cf. Eqs. (30), (67)) by:

$$\delta E_\pi = \frac{\partial E_\pi}{\partial \alpha_i} \delta \alpha_i = q_i \delta \alpha_i \quad (101)$$

where $\delta \alpha_i$ is the change in the coulomb integral of nitrogen atom i on forming the salt. To a first approximation, q_i will have the

same value that it does in the isoconjugate AH. This value is of course unity if the AH is even. If it is odd, as in the case of a base such as aminopyridine which is isoconjugate with the benzyl anion, i.e.



then q_N can be calculated approximately from Eq. (68):

$$q_i = 1 + a_{oi}^2 \quad (103)$$

Hence the basic dissociation constant K_B should follow the relation—

$$-RT \log K_B = C + \delta E_\pi = C(1 + a_{oi}^2)\delta\alpha_i \quad (104)$$

where C is a constant for a given solvent, temperature, etc. Thus a plot of $\text{p}K_B$ for the bases against a_{oi}^2 should be a straight line; Longuet-Higgins¹⁵ has shown the relation to hold quite well for a wide range of bases. An interesting and surprising conclusion is that even alternant bases such as pyridine, quinoline, acridine, etc., should all have similar basic strengths since $q_i = 1$ at each position in the isoconjugate AH; this is found to be the case in practice.

Of course one can calculate q_i for the heterocyclic bases directly and use this value in Eq. (101); and one can put in additional corrections for the interaction between the positively charged 'onium center and charges on more distant atoms. Procedures of this kind are essential in molecules which are non-alternant or contain many heteroatoms. Pullman and Pullman³⁴ have carried out numerous calculations of this kind for heteroaromatic bases of importance in biology and have found a good general agreement with experiment, even though they used the simple Hückel approximation—a rather dubious procedure in cases of this kind. Daudel and his collaborators³⁵ have pointed out that such calculations give widely varying values for q_i in the case of simple heteroaromatic bases such as pyridine, quinoline, etc.; these values would imply a wide variation in basic strength which is not in fact observed. These points will be discussed in more detail later (Section XIV).

The second kind of situation is illustrated by side-chain reactions of benzene where the reaction center is not significantly

linked to the π electrons of the ring. In these cases the rate of reactions can be varied by introducing substituents into the ring; some time ago Hammett³⁶ showed that the effect of the substituent on the rate was given by the relation

$$\log (k/k_0) = \rho\sigma$$

where k_0 is the rate constant for the unsubstituted reactant, ρ is a constant characteristic of the reaction, and σ one characteristic of the substituent. It is now generally agreed that this relation holds only in cases where there is no direct resonance interaction between the substituent and the reaction center;³⁷ the effect on the rate is then due to the electric fields set up at the reaction center by charges induced in the ring by the substituent. Thus the ionization of benzoic acid,



is facilitated by substituents that set up positive electric charges on the ring; these decrease the energy of the delocalized electrons on the carboxylate group by a direct electrostatic attraction.

The philosophy of perturbation theory is to consider the whole group of reactants undergoing a given reaction as variations on a central theme. We have seen how this principle is applied to heteroatomic systems by regarding them as perturbed forms of the isoconjugate hydrocarbons; likewise it is convenient to treat as many such molecules as possible in terms of a fixed kernel with varying substituents attached to it. This is indeed the procedure commonly followed in chemistry, confirming the view that chemistry is in effect an exercise in perturbation theory. Our next problem then is to consider how substituents may influence reactivity.

If the reaction involves a conjugated system, and if the substituent is attached directly to it and can conjugate with it, then of course there will be a direct effect on δE_π or δE_π^\ddagger . This can either be estimated by direct calculation of E_π for the whole system including the substituent or, more logically, it can be deduced from the value $(\delta E_\pi)_0$ or $(\delta E_\pi^\ddagger)_0$ for the corresponding unsubstituted system by treating the introduction of the substituent as a perturbation and by using perturbation theory.

The problem here involves the union of two conjugated systems,

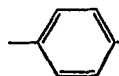
one that of the substrate, one that of the substituent. This can be solved very simply by using Eqs. (50) and (55), and in this way a complete theory of such substituent effects can be developed. Full details will be found in a series of papers¹⁴ to which reference has already been made; the qualitative results can be summed up very simply as follows.

Electromeric substituents (i.e. those containing p or π electrons and able to interact with adjacent conjugated systems) can be divided into three classes:

(a) $\pm E$ substituents; these are radicals derived from even AH's, e.g. vinyl, phenyl, naphthyl.

(b) $+E$ substituents; these are substituents isoconjugate with $\pm E$ substituents but containing heteroatoms more electronegative than carbon; formyl (isoconjugate with vinyl) and γ -pyridyl (isoconjugate with phenyl) are examples.

(c) $-E$ substituents; these are radical derived from odd AH anions, or compounds isoconjugate with such anions, and attached through an active atom (i.e. one in which the NBMO of the AH has a non-vanishing coefficient). Examples are $-\text{CH}_2^-$, $-\text{OMe}$,



$-\text{NMe}_2$. Substituents of this kind attached through an inactive atom are classed as $\pm E$ or $+E$ substituents, depending on whether or not they contain heteroatoms. Thus the groups $-\text{NO}_2$, $-\text{COOEt}$ are $+E$ substituents even though they are both isoconjugate with the allyl negative ion.

We can now give a table showing the qualitative effects of substituents on the stabilities of various types of conjugated systems.

TABLE III. Effect of Electromeric Substituents on Conjugated Systems

Relative stabilizing effect of substituent on:				
Substituent	even AH	odd AH anion	odd AH radical	odd AH cation
$\pm E$	small	large	large	large
$+E$	small	very large	large	?
$-E$	small	small	moderate	very large

The effect of the substituent on an odd AH is roughly proportional to the square of the non-bonding MO coefficient at the point of attachment; substituents attached at inactive positions have little effect. Note that the effect on even AH's is small; substituents have most effect on reactions that involve a change in the size of a conjugated system, reactions where we proceed either from an even system to an odd one, or from odd to even. The effect of the substituent appears mainly in the odd member of the pair. It is very easily seen that these rules are equivalent to those given by resonance theory but this treatment has the advantage of being easily put in a quantitative form.¹⁴ One point is of interest: the effect of +E substituents on odd AH cations. This turns out to be ambiguous, depending on the magnitude of two contributing terms of opposite signs. Substituents of this kind do indeed show ambiguous effects, and a more detailed analysis shows that these can very easily be explained in terms of the relative magnitudes of the two contributing terms. In this way one can solve one of the classic riddles of organic chemistry, why it is that some substituents of this kind (e.g. NO₂, CHO) direct electrophilic substitution into the positions *meta* to them in benzene, while others (e.g. —CH=CH—COOEt) are *ortho*:*para* directing. It turns out that the smaller +E substituents destabilize odd AH cations, such as the benzenonium ion intermediate in electrophilic substitution, while large ones have a stabilizing effect; these effects can of course occur only if the substituent is at an active site in the ion, i.e. if it is *ortho* or *para* to the point of attack.

We are left with the problem of substituent effects that do not depend on direct mesomeric interactions between the substituent and the reaction center. Effects of this kind can arise in one of two ways. First, the bond between the substituent and the substrate may be polar, and there may also be polar bonds or charged atoms in the substituent itself; the charges set up in this way can influence the reaction center either by altering the effective electronegativity of atoms connected with it (inductive effect) or by direct electrostatic interaction across space (field effect). Secondly, the substituent may be attached to a conjugated system which does not itself take part in the reaction, the case exemplified by the Hammett equation (Eq. (105)); here π

interactions between the substituent and the adjacent conjugated system may lead to a polarization of the π electrons, the resulting charges influencing the reaction center by a secondary inductive or field effect.

It used to be thought that the inductive effect could be propagated by successive polarization of intervening σ bonds between the substituent and reaction center, but a recent study³⁸ has shown that this is not the case. All the long range effects of substituents appear to be transmitted either by polarization of intervening π -electron systems or directly across space (field effect). So far the magnitudes of these two effects have been calculated³⁸ only to a primitive first approximation. The field effect was assumed to vary inversely as the distance between the substituent and the reaction center. The resonance polarization was estimated by assuming it to be proportional to that brought about by the substituent $-\text{CH}_2^-$; when this is attached to an even AH, the product is an odd AH anion in which the formal negative charge at each position is a measure of the polarization induced by the substituent $-\text{CH}_2^-$. This can of course be estimated at once from Eq. (68). The charge (δq_i) at position j is given by:

$$\delta q_j = a_{oj}^2 \quad (107)$$

where a_{oj} is the NBMO coefficient at atom j in the odd AH formed by adding CH_2 to position i of the original even AH. The corresponding charge at position j produced by some other substituent at atom i will then be $M_s a_{oj}^2$, where M_s is a constant characteristic of the substituent S and serves as a measure of its conjugating power. With these assumptions we arrive at an estimate of the total field (σ_{ij}) at position j , due to our substituent in position i —

$$\sigma_{ij} = F_s/r_{ij} + M_s a_{oj}^2 \quad (108)$$

Now the sensitivity of the reaction center to an applied field of this kind is given by the corresponding Hammett ρ constant; in this way we obtain an extended form of the Hammett equation,

$$\log (k/k_0) = \rho(F_s/r_{ij} + M_s a_{oj}^2) \quad (109)$$

Here ρ is constant for a given reaction center attached to any AH, while F_s , M_s are constants characteristic of the substituent and again independent of the substrate to which it is attached.

These constants can be determined empirically from data for benzene and then used to calculate rates in other ring systems; the available data fit Eq. (101) remarkably well.

This approach is clearly preferable to the purely empirical treatments of substituent effects that have been popular in recent years. The actual execution indicated above is of course very primitive and there are obvious ways in which it could and should be extended and refined.

X. OTHER CRITERIA OF REACTIVITY

The sole factor determining the value of a rate or equilibrium constant is the difference in free energy between the reactants and either a transition state, in the case of a reaction rate, or the products, in the case of an equilibrium. Rate and equilibrium constants cannot therefore properly be correlated with any static property of the reactants themselves. This point cannot be emphasized too strongly in view of the many attempts that have been made to find such correlations. One might add that attempts of this kind are in any case basically unsatisfactory in that they ignore the transition state entirely and so can throw no light on its structure; even if correlations of this kind can be established, they do not throw any light on the detailed mechanism of chemical process—and it is just in this field that quantum theory has most to offer to chemists.

We have already considered one criterion of this kind, the free valence number; here we shall consider three other properties of molecules which have been used in similar connections. These are the charge density, self-polarizability, and frontier orbital density. All of these properties show correlations with reactivity, at least in certain ranges of compounds, but these correlations are due in each case to fortuitous correspondences between them and the quantities δE_D or δE_b^* —the same situation that arises in the case of free valence number.

A. Charge Density

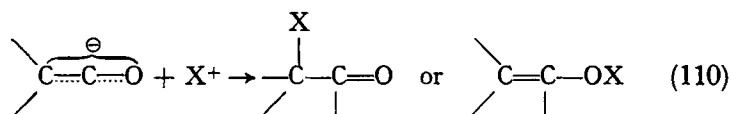
The use of charge density as a criterion is based on another time-honored chemical idea, the electrostatic theory of reactivity.

In a reaction involving attack by an ion on a neutral but polar molecule, or in a reaction between two polar molecules, it seems intuitively obvious that the rate should be influenced by the mutual coulombic interactions between the reagents. Thus in electrophilic substitution of a neutral aromatic compound by a positively charged electrophile (e.g. NO_2^+), one might expect attack to take place most readily at the most negative position in the molecule. This idea was developed some time ago by Ri and Eyring,³⁹ the charges being estimated by a simple resonance treatment; in recent applications, however, the charge distributions have usually been calculated by some variant of the MO method. Numerous calculations of this kind have been reported,¹³ particularly for heteroaromatic compounds, and the results have been used to interpret and predict orientation of substitution in aromatic systems of various kinds.

The use of charge density in this way is of course incorrect and although it often works quite well in practice, it is not hard to find glaring exceptions. Classic examples of this are provided by cinnamic acid (IX), ω -nitrostyrene (X), and γ -phenylpyridine (XI). These compounds undergo electrophilic substitution in the benzenoid ring mainly in positions *ortho:para* to the substituent, whereas the π -electron density is calculated in each case to be higher at the *meta* position. The reason for this is simple. Charge density can serve as a criterion of reactivity only in isoconjugate reactions (Section IX) where there is no change in the structure of the conjugated system during the reaction. Thus the π -electron density on nitrogen does serve as a good indication of basicity in heterocyclic bases (cf. Eq. (101)); here the reaction in question leaves the conjugated system of the base qualitatively unchanged. Aromatic substitution is not an isoconjugate reaction.

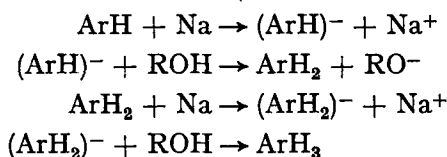
One special case is provided by very fast reactions where the activation energies are low and where the transition states consequently resemble the reactants closely; here the transition state may be so nearly isoconjugate with the reactants that charge density may serve as a good measure of reactivity. A good example is provided by the reaction of electrophiles X^+ with mesomeric anions where two or more products can be formed by attachment of the electrophile at different points; thus the

conjugate base of a ketone can react with a proton to give either a ketone or an isomeric enol:

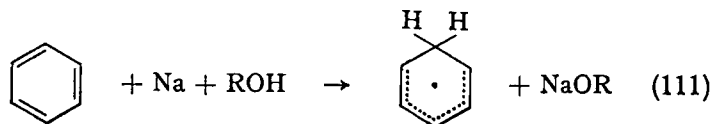


If X^+ is a very reactive electrophile, e.g. H^+ , reaction takes place at the most negative atom in the mesomeric ion; thus enolate ions react with acids to give enols as primary products, H^+ being a very strong electrophile. If on the other hand X^+ is a weak electrophile, the choice of product is determined by the relative stabilities of the two products; thus enolate ions react with alkyl halides to give ketones rather than the less stable isomeric enol ethers. Here the transition state is intermediate in structure between reactants and products and the charge distribution in the reactants no longer controls the course of the reaction. A detailed discussion of this point in terms of potential energy surfaces will be found in a note by the author;⁴⁰ Kornblum⁴¹ has made much use of this idea in interpreting the reactions of mesomeric ions.

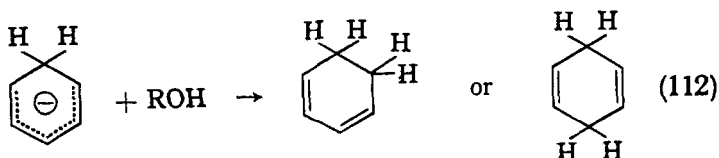
An interesting example, and the one where these ideas were first applied,⁴⁰ is the Birch reduction of aromatic compounds by sodium in liquid ammonia containing alcohol. These reactions seem to take place by two successive electron transfers, each followed by capture of a proton, i.e.



In the case of benzene the intermediate ArH_2 is a benzenonium radical:



The corresponding anion can react with alcohol in one of two ways to give either a 1,3- or 1,4-diene:



The question is, which diene will be formed? If the stability of the products were a determining factor, one might expect to find comparable amounts of the two products; for contrary to what one might have expected from analogy with open chain dienes, the two isomeric cyclohexadienes are in fact of comparable stability.⁴² However, the reaction involves protonation of a carbanion, and this should be a case where the transition state resembles the reactants so closely that charge density should be a dominating factor. It is true that the simple Hückel theory predicts equal formal charges at the positions *o:p* to methylene (Fig. 3a); however, calculations by the SCF MO method indicate that the *para* carbon should carry the greater charge. The charges calculated by the Pople method are shown in Fig. 3b. In practice the sole isolable product from the reaction is the 1,4-diene.

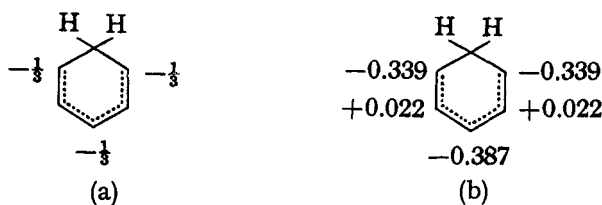


Fig. 3. Distribution of formal charge in the anionic intermediate of the Birch reduction of benzene; calculated (a) by the Hückel method, (b) by the Pople method.

Although the use of charge density as a criterion of reactivity in other cases is theoretically unsound, the correlation between the two is often quite good and this procedure has been much used. We may therefore examine the matter more closely to

see why such a correlation should exist. We shall consider the specific case of substitution in a heteroaromatic compound containing a single heteroatom; the argument can easily be generalized to compounds containing several heteroatoms since it is based on the use of first order perturbation theory and first order perturbations are additive.

Denote by R' the AH isoconjugate with the heteroaromatic compound R . In R' the charge density at each atom is unity. Consider the charge density, q_i , at position i in R . If the heteroatom is at position i , and if its coulomb integral relative to carbon is $\delta\alpha_i$, then to a first approximation—

$$q_j = 1 + \pi_{j,i}\delta\alpha_i \quad (113)$$

where $\pi_{j,i}$ is the atom-atom polarizability¹⁹ of atoms j, i in R' . We can estimate $\pi_{j,i}$ approximately as follows. Consider the odd AH S formed from R by loss of atom i (Fig. 4). When we reconstruct R by uniting S with this atom, all the MO's of R remain unchanged in a first approximation, except for the NBMO Φ_0 .

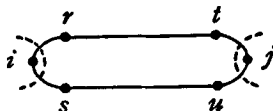


Fig. 4. Dissection of R by excision of atom i to give S , or of atom j to give T .

This interacts with the AO ψ of atom i to form a combined orbital $\frac{1}{\sqrt{2}}(\Phi_0 + \psi)$ (cf. Eq. (56)). Now suppose we make atom i very slightly more electronegative than carbon, changing its coulomb integral by a small amount $\delta\alpha_i$. The only important interaction between the MO's of S and the AO ψ will still be that involving the NBMO Φ_0 of S ; however the perturbed orbital will now differ from zero in energy and it will no longer be formed equally from Φ_0 and ψ . The energies are given by the secular equation:

$$\begin{vmatrix} (\delta\alpha_i - E) & (a_{or} + a_{os})\beta \\ (a_{or} + a_{os})\beta & -E \end{vmatrix} = 0 \quad (114)$$

where a_{or} , a_{os} are the NBMO coefficients of the atoms adjacent to atom i in R. The orbitals are of the form

$$A_1\psi + A_2\Phi_0 \quad (115)$$

where

$$A_1(\delta\alpha_i - E) + A_2\beta(a_{or} + a_{os}) = 0 \quad (116)$$

Neglecting terms in $(\delta\alpha)^2$, the solutions of Eqs. (114) and (116) are:

$$E = \frac{1}{2}\delta\alpha_i \pm (a_{or} + a_{os})\beta \quad (117)$$

$$A_1^2 = \frac{1}{2} \left(1 + \frac{\delta\alpha_i}{2\beta(a_{or} + a_{os})} \right) \quad (118)$$

$$A_2^2 = \frac{1}{2} \left(1 - \frac{\delta\alpha_i}{2\beta(a_{or} + a_{os})} \right) \quad (119)$$

The MO Φ'_0 of R formed by interaction of S with atom i is given by:

$$\begin{aligned} \Phi'_0 &= A_1\psi + A_2\Phi_0 \\ &= A_1\psi + A_2\sum_k a_{ok}\varphi_k \end{aligned} \quad (120)$$

Since the other MO's of S survive unchanged in R, to this first approximation, the π -electron density q_j at atom j is given by:

$$\begin{aligned} q_j &= 2 \sum_{m \neq 0}^{\text{occ}} a_{mj}^2 + 2A_2^2 a_{oj}^2 \\ &= 2 \sum_{m \neq 0}^{\text{occ}} a_{mj}^2 + a_{oj}^2 \left(1 - \frac{\delta\alpha_i}{2\beta(a_{or} + a_{os})} \right) \end{aligned} \quad (121)$$

If $\delta\alpha_i = 0$, $q_j = 1$; hence:

$$q_j = 1 - \frac{a_{oj}^2 \delta\alpha_i}{2\beta(a_{or} + a_{os})} \quad (122)$$

Comparison with Eq. (113) shows that:

$$\pi_{j,i} = - \frac{a_{oj}^2}{2\beta(a_{or} + a_{os})} \quad (123)$$

Now consider electrophilic substitution in R at atom j . The Wheland intermediate T is derived from R by excision of atom j (Fig. 3). The π -electron density at atom i in S' is given by

$$q'_i = 1 - (a'_{oi})^2 \quad (124)$$

where a'_{oi} is the NBMO coefficient of atom i and S'. If the atoms adjacent to atom j are atoms t, u then from analogy with Eq. (123),

$$\pi_{i,j} = - \frac{(a'_{oi})^2}{2\beta(a'_{or} + a'_{os})} \quad (125)$$

Hence from Eqs. (63), (124) and (125),

$$q'_i = 1 + \beta N_j \pi_{i,j} \quad (126)$$

Where N_j is the reactivity number of atom j . But it can be shown¹⁹ that

$$\pi_{i,j} = \pi_{j,i} \quad (127)$$

Hence

$$q'_i = 1 + \beta N_j \pi_{j,i} \quad (128)$$

From Eq. (113), the formal charge (δq_j) on atom j in R is given by:

$$\delta q_j = \pi_{i,j} \delta \alpha_i \quad (129)$$

The formal charge (δq_i) on atom i in the Wheland intermediate T is given by

$$\begin{aligned} \delta q'_i &= \beta N_j \pi_{j,i} \\ &= \frac{\beta N_j}{\delta \alpha_i} \delta q_j \end{aligned} \quad (130)$$

The arguments of Section V show that the π energy of activation, δE_π^\ddagger , for substitution of atom j in R is given in terms of that, $(\delta E_\pi^\ddagger)_0$, for corresponding substitution in the isoconjugate AH by:

$$\delta E_\pi^\ddagger = (\delta E_\pi^\ddagger)_0 - \delta q_i \delta \alpha_i \quad (131)$$

From Eqs. (130) and (131),

$$\delta E_\pi^\ddagger = (\delta E_\pi^\ddagger)_0 + \beta N_j \delta q_j \quad (132)$$

The charge density is therefore not a measure of reactivity *per se*, but of the difference in reactivity between a given heteroatomic system and the isoconjugate hydrocarbon. The expression

for the π energy of activation for electrophilic or nucleophilic substitution in an alternant heteroaromatic compound can be divided into two terms (Eqs. (69)–(71)); the first is the energy for substitution in the isoconjugate AH, the second a correction to this for the effect of the heteroatoms. The static charge distribution in a heteroaromatic molecule is a measure only of the second factor. As long as this is dominant, or as long as there is some fortuitous correlation between the two factors, the charge density may serve as a measure of reactivity. However, it can do so only by virtue of some such coincidence.

B. Self-polarizability

Charge density cannot be used as a measure of reactivity in the case of AH's since here $q_i = 1$ at each position. Coulson and Longuet-Higgins¹⁹ suggested that the self-polarizability might be used instead. The self-polarizability ($\pi_{i,i}$) of atom i is a measure of the way the charge of atom i changes with changes in its coulomb integral:

$$q_i = 1 + \delta q_i = 1 + \pi_{i,i} \delta \alpha_i \quad (133)$$

The approach of a charged reagent will set up an electrostatic potential at atom i and so alter its effective electronegativity; the resulting induced charge may then assist attack by the reagent. There is indeed a good correlation¹³ between reactivity and self-polarizability in AH's, comparable with the analogous correlations involving π energy of activation or free valence number.

The reason for this is easily seen. Using the same model as in the previous section (Fig. 4), the π -electron density at atom i is seen to be given by:

$$q_i = 2A_i^2 \quad (134)$$

$$= 1 + \frac{\delta \alpha_i}{2\beta(a_{or} + a_{os})} \quad (135)$$

Comparison with Eq. (133) shows that:

$$\pi_{i,i} = \frac{1}{2\beta(a_{or} + a_{os})} \quad (136)$$

Using Eq. (63),

$$\pi_{i,i} = \frac{1}{\beta N_i} \quad (137)$$

From Eq. (64),

$$-RT \log (k/k_0) = \frac{1}{(\pi_{i,i})_0} - \frac{1}{\pi_{i,i}} \quad (138)$$

There is therefore a correlation between the rate and the reciprocal of the self-polarizability, due to this accidental first-order correspondence between it and the reactivity number. The correlation does not in any way support the physical model on which it was originally based.

C. Frontier-electron Density

Fukui⁴³ has introduced yet another measure of reactivity, the frontier-electron density. The frontier electrons are those occupying the filled orbital of highest energy; the idea is that in any interaction with an external agent this orbital should be perturbed more strongly than the rest. It is very difficult to see any good justification for this assumption. There is, it is true, a good correlation between frontier orbital density and reactivity in even AH's but this again is due to an accidental correspondence between frontier orbital density and localization energy. The correlation breaks down badly in the case of heterocyclic systems; in any case it is difficult to generalize the treatment in any satisfactory way to account for the different orientations observed in such cases with reagents of different types.

D. Comparison of the Various Criteria of Reactivity

All criteria of reactivity work well for even AH's, in which the π electrons are evenly distributed, owing to the fortuitous correlations that have been pointed out above. In order to get a real test of their empirical effectiveness, one should choose some compound in which the π electrons are very evenly distributed. Recently⁴⁴ a whole new range of aromatic compounds have become available containing boron; over twenty ring-systems of this kind have now been prepared. These compounds

are isoconjugate with even AH's, but the π -electron distributions in them are very strongly perturbed; they provide an ideal testing ground for chemical theories. Figure 5 shows PMO localization energies for one of these ring systems, 10,9-borazarophenanthrene, together with charge densities and frontier orbital coefficients calculated by the Pople method.

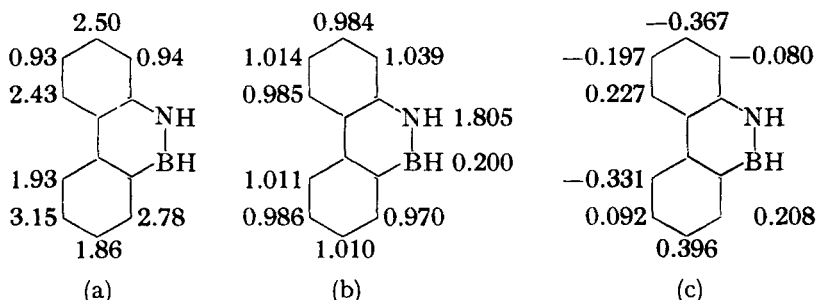


Fig. 5. Calculations for 10,9-borazarophenanthrene. (a) PMO localization energies ($\times \beta^{-1}$); (b) π -electron densities; (c) frontier orbital coefficients.

It will be seen that the π -electron distribution seems indeed to be uneven, the nitrogen being estimated to have 1.8 π electrons and the boron but 0.2. Electrophilic substitution takes place very much more readily in the 6- and 8-positions than anywhere else; the 2-position is the third most reactive. The 8-position is somewhat more reactive than the 6-position but the difference is very much less than that between the 6- and 2-positions. It will be seen that the simple PMO estimates of δE_{π}^{\dagger} give a very good account of substitution in this system, given that the 4-position, like that in phenanthrene, must be sterically hindered. These calculations correctly predicted the orientation of the products for us before we had established this experimentally; indeed we were assisted in devising chemical proofs of their structures by this foreknowledge.

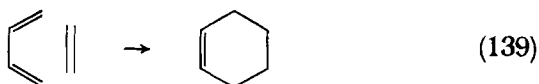
The π -electron density is much higher at position 8 than at any other, leading to the correct prediction that the 8-position should be the most reactive. The π -electron density at the 6-position is the second highest, but it is very much less than that at the 8-position and very little more than that at the 2-position; this does not agree with the observed reactivities. The frontier orbital

coefficients bear no relation at all to the observed reactivity; indeed the smallest coefficient of all is at the most reactive position.

XI. REACTIONS INVOLVING CYCLIC TRANSITION STATES

The majority of chemical reactions involve the breaking and/or formation of just one bond; reactions of this kind are analogous to one or other of the two main types of reactions discussed above (aromatic and aliphatic substitutions) and can be treated in an exactly similar manner. In each case the transition state differs from the reactants in having one more, or one less, atom participating in the delocalized system; δE_b^\ddagger is then the energy required to remove one atom from the delocalized system or to add one atom to it. There is also in many cases the possible additional complication that bonds may be only partially formed or broken in the transition state. The examples given above show how this can also be taken into account and an estimate given of the extent to which bond breaking and bond formation has proceeded in the transition state.

A number of reactions are known, however, in which more extensive rearrangements of bonds occur and which involve cyclic intermediates or products. The Diels-Alder reaction is a classical example of this. In the normal Diels-Alder reaction a *cis*-1,3-diene reacts with an ethylene derivative (dienophile) to form a cyclohexene:



A number of similar reactions are also known in which the product is a cyclobutane, e.g.

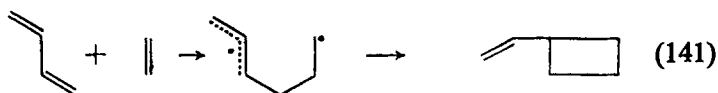


In these reactions two bonds are broken and two are formed. The bonds broken are π bonds, the bonds formed σ bonds; the

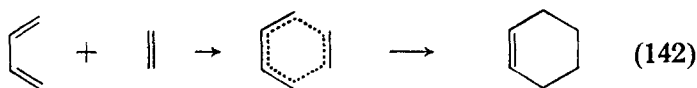
driving force in the reaction is the greater heat of formation of σ bonds compared with π bonds.

Two questions immediately arise. First, why do some of these reactions lead to cyclohexenes and others to cyclobutanes? And secondly, are the two new bonds formed simultaneously in one step or separately in two distinct steps?

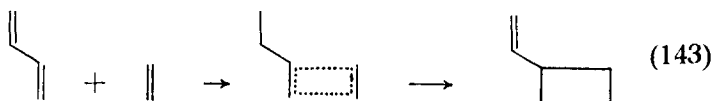
If the reaction took place in two steps via an intermediate biradical, one might expect the cyclobutane to be preferred; for here the butadiene could react in its more stable *trans* form, and moreover the transition state for cyclization to a cyclobutane would have more flexibility and so a higher entropy:



The preferential formation of cyclohexene from the less stable *cis* isomer can only be satisfactorily explained if both the new bonds are indeed formed simultaneously, the transition state being cyclic:



One has of course to explain why a similar cyclic transition state does not lead to the formation of a cyclobutane:

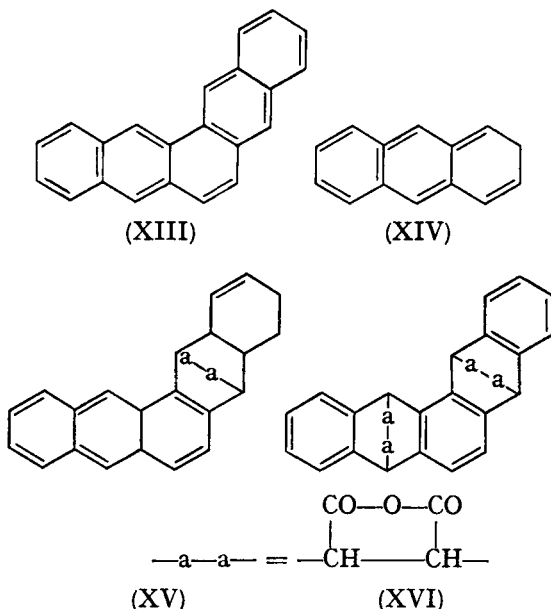


The dotted lines in the transition states represent delocalized MO's formed by interaction either of six AO's on six adjacent atoms or of four AO's on four adjacent atoms. The situation is qualitatively similar to that in benzene or cyclobutadiene. Now the π energy of benzene is lower than that of 1,3,5-cyclohexatriene, whereas that of cyclobutadiene is probably higher than that of

1,3-butadiene; the six-membered cyclic transition state in Eq. (142) should therefore have a lower E_D than the open-chain transition state of Eq. (141), whereas the four-membered cyclic transition state of Eq. (143) should have a higher E_D . There is therefore an advantage in forming the two new bonds simultaneously, but only if the product is a cyclohexene. The six-membered cyclic transition state is indeed aromatic, as Evans⁴⁵ first pointed out. The choice between cyclohexene and cyclobutane rests on whether the extra gain in delocalization energy in forming the aromatic transition state outweighs the loss in entropy and steric restraints involved.

There has been considerable controversy⁴⁶ concerning the mechanism of the "normal" Diels-Alder reaction leading to cyclohexenes; the arguments given above support very strongly the idea that it takes place in one step. Further evidence for this is provided by calculations of the relative reactivities of aromatic dienes. If the two-step mechanism of Eq. (141) were correct, the rate-determining step in the reaction of an aromatic diene could be regarded as a simple aromatic substitution process and its rate be determined by the reactivity number at the point of preliminary attack (Eq. (64)). If, however, attack takes place simultaneously at two points in the ring, the rate-determining reaction is one that removes *two* atoms from conjugation. If the transition state resembles the products closely, δE_7^\ddagger for the reaction will then be the difference in π energy between the reactants and a compound with two fewer conjugated atoms. Since the carbon atoms in question are *para* to each other in the case of an aromatic diene, Brown⁴⁷ has termed the corresponding value of δE_7^\ddagger the *paralocalization energy*. Brown calculated δE_7^\ddagger for a number of aromatic systems and was able to show that the rates of reaction do indeed seem to run parallel to it. A very pretty example is provided by pentaphene (XIII), which has a higher paralocalization energy than anthracene (XIV). Since reaction of XIII with a dienophile, e.g. maleic anhydride, gives an anthracene derivative (XV), and since anthracene has a lower paralocalization energy than XIII, we would expect XV to react faster with a second molecule of dienophile than did XIII with the first. If then we allow XIII to react with one mole of maleic anhydride, the product should consist mainly of equal amounts of unchanged XIII and

the double adduct XVI; this is what is observed—indeed, the monoadduct has not yet been isolated from this reaction.



The paralocalization energies can also be estimated¹⁴ by the simple PMO method. To a first approximation, the energy (P_{ij}) required to remove two atoms simultaneously from a conjugated system is given by:

$$P_{ij} = \beta(N_i + N_j) \quad (144)$$

where N_i , N_j are the corresponding reactivity numbers.

Now, of course, the transition state in fact has a structure intermediate between the reactants and products; the situation is the same as in aromatic substitution where the transition state lies between the reactants and the arenonium intermediate. This can be allowed for by an exactly similar procedure. If the bonds to atoms i , j are formed to an equal extent in the transition state, then

$$\delta E_{\pi}^{\ddagger} = \epsilon P_{ij} = \epsilon \beta(N_i + N_j) \quad (145)$$

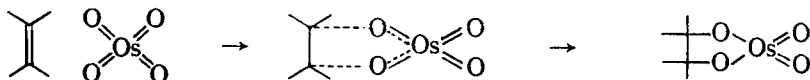
where ε is a proportionality factor whose value determines how closely the transition state resembles the product.

There is, however, no reason why the two new bonds should be formed to the same extent in the transition state, and recent studies⁴⁶ have suggested that this is not in fact the case. It seems very likely that the transition state has an unsymmetrical structure in which the two new bonds are formed to an unequal extent. In that case we would expect—

$$\delta E_{\pi}^{\ddagger} = \beta(\varepsilon_1 N_1 + \varepsilon_2 N_2) \quad (146)$$

where the proportionality factors ε_1 , ε_2 are measures of the extent to which the new bonds are formed in the transition state and their ratio a measure of the asymmetry.

A second class of reactions of this kind are ones involving cycloaddition to double bonds. The Diels–Alder reaction can be regarded as an example if we are concerned primarily with the fate of the dienophile. It is generally believed that various oxidations of olefins, e.g. by osmium tetroxide, also take place in this way, i.e.



If the double bond forms part of a conjugated system, the overall reaction has the effect of simultaneously removing two adjacent carbon atoms from it. If the system in question is aromatic, the atoms will be *ortho* to one another. Brown⁴⁷ has therefore called the corresponding change in π energy the *ortholocalization energy*. He has shown that this runs parallel to the rates of oxidation of various aromatic hydrocarbons by reagents of this type. Here again the ortholocalization energy can be calculated by using simple perturbation theory.¹⁴ If the two atoms in question are r , s , then the ortholocalization energy O_{rs} is given approximately by:

$$O_{rs} = \beta(N_r + N_s - 2p_{rs}) \quad (147)$$

where N_r , N_s are the corresponding reactivity numbers and p_{rs} the bond order of the bond between atoms r , s . Here again careful and detailed comparison of ortholocalization energies with

rates of reaction could give much information concerning the structure of the transition state.

It is very difficult to devise experiments by which the mechanisms of reactions of this class can be established; they have for this reason been described, not altogether frivolously, as "no-mechanism" reactions. Investigations along the lines indicated above could well resolve these problems. For this one would need extensive data for reactions involving aromatic and conjugated hydrocarbons of varying size and shape and free from extraneous substituents. Data of this kind are lacking, probably mainly because the need has not been recognized.

XII. THE LOCALIZED BOND MODEL

We have assumed a classical model for molecules in which the majority of the electrons are localized on definite atoms or in definite two center bonds. Although this assumption works well in practice, it certainly needs justification, for in a correct LCAO MO description of a typical molecule, each MO is composed of AO's contributed by all the atoms present and there is nothing in this description that corresponds even remotely to the classical idea of localized bonds.

The situation can be clarified by the following argument⁴⁸ based on a simple perturbational approach. Suppose we first represent the wave function of the molecule in terms of "classical" MO's, each built up from a pair of AO's of two adjacent atoms. Such MO's will of course appear in pairs, one bonding, the other antibonding; in each case the bonding MO will be occupied and the antibonding MO empty. The orbitals will then fall into groups, the orbitals in each group having the same energy; denote the orbitals of the n th group by ψ_{ni} ($i = 1, 2, \dots$) and their energies by E_n .

Suppose now that we allow the orbitals to interact. The ultimate result will be a scrambling of the orbitals to give in the end the same set of many-center MO's that would be obtained by a normal LCAO MO treatment.⁴⁹ Let us, however, consider the interactions in terms of perturbation theory. There will be a first order perturbation to the degenerate set of MO's ψ_{ni} due to their mutual interaction. Writing the perturbed energy of the

i th orbital as $E_n + \xi_{ni}$, the perturbation ξ_{ni} will be one of the roots of the secular equation:

$$\det | P_{nijn} - \xi \delta_{ij} | = 0 \quad (148)$$

Here P_{nijn} is a matrix element of the operator \mathbf{P} that represents the interactions between the orbitals:

$$P_{nijn} = \int \psi_{ni} \mathbf{P} \psi_{nj} d\tau \quad (149)$$

As usual we neglect overlap. Equation (148) can be expanded in descending powers of E :

$$\xi^k - \sum_{i < j} P_{ij} \xi^{k-2} + \dots = 0 \quad (150)$$

where k is the total number of MO's ψ_{ni} . In this equation the term in ξ^{k-1} vanishes; hence the sum of the roots of the equation vanishes.

Now the set of MO's ψ_{ni} is either fully occupied or empty in the original classical structure, depending on whether the orbitals ψ_{ni} are bonding or antibonding. In the final structure, the orbitals corresponding to ψ_{ni} will likewise either all be full or all be empty. Empty orbitals do not of course contribute to the total energy of the molecule. If the orbitals ψ_{ni} are filled, the total energies F_n , F'_n of the electrons occupying them in the unperturbed and perturbed systems are:

$$F_n = 2kE_n \quad (151)$$

$$F'_n = 2 \sum_i (E_n + \xi_{ni}) = 2kE_n + 2 \sum_i \xi_{ni} = 2kE_n = F_n \quad (152)$$

Therefore although the first order perturbations may greatly alter the energies of the individual MO's of the set ψ_{ni} , they do not alter the *total* energy of the electrons occupying them. It can be shown likewise that the total electron distribution also remains unchanged.

Now consider a second order interaction between two MO's ψ_{mi} , ψ_{nj} from two different sets. Their energies, including the first order perturbations, are given by $E_m + \xi_{mi}$ and $E_n + \xi_{nj}$. The second order perturbed energies E'_{mi} , E'_{nj} are then given by:

$$E'_{mi} = E_m + \xi_{mi} + \frac{P_{minj}^2}{E_m + \xi_{mi} - E_n - \xi_{nj}} \quad (153)$$

$$E'_{nj} = E_n + \xi_{nj} + \frac{P_{minj}^2}{E_n + \xi_{nj} - E_m - \xi_{mi}} \quad (154)$$

Hence:

$$E'_{mi} + E'_{nj} = (E_m + \xi_{mi}) + (E_n + \xi_{nj}) \quad (155)$$

The second order perturbations again fail to affect the total energy of the interacting orbitals. If the orbitals ψ_{mi} , ψ_{nj} are occupied in the unperturbed system, their mutual interactions have no effect on the total energy of the electrons occupying them.

Thus the only interactions that can alter the total energy of the molecule are those between filled bonding orbitals and empty antibonding orbitals. Since these differ greatly in energy, the corresponding second order perturbations will be relatively small, for the energy difference $E_m - E_n$ appears in the denominator of the expression for the perturbation (Eq. (153)).

This argument shows that the effect of the interactions on the total energy of the molecule will be much less than its effect on the energies of the individual orbitals. If we are concerned only with *collective properties* of the molecule (i.e. those that depend collectively on all the electrons taken together), and if the interactions between the localized orbitals in the classical model are not too large, then the localized bond picture may provide a satisfactory description of the molecule in the sense that the molecule behaves almost as if the electrons in it did in fact occupy localized orbitals. This situation holds in the case of chemical reactivity; chemical reactivity depends only on the total energies of molecules and of transition states.

Whether or not the localized bond model will be sufficiently accurate in any given case can of course be determined only by experiment, for existing *a priori* quantum chemical methods cannot be applied to problems of such complexity. Experiment⁶ implies that the localized bond model works well for all classical molecules, i.e. molecules for which only single classical structures can be written. Here the localization is probably assisted by correlation effects that tend to concentrate the electrons in pairs in definite two-center bonds.

The localized bond model fails for odd conjugated systems (ions and radicals such as allyl or benzyl); the mesomeric stabilization of these can be estimated by the perturbation treatment of Section VIII. However, the localized bond model can still⁴ be used for other types of odd systems, i.e. ones where the

delocalization would correspond to a hyperconjugative interaction; for chemical purposes the stabilizing effect of an alkyl substituent on a radical or carbonium ion can be attributed to changes in bond energy with hybridization⁵ or to an inductive effect.^{4b}

The only other types of system to be considered are those with multicenter bonds other than π bonds, and non-classical even conjugated systems. Most examples of multicenter bonds involve three-center orbitals formed by mutual overlapping of AO's of three different atoms; diborane and the transition state of an S_N2 reaction, provide good examples. An even conjugated system can have more than one classical structure only if it is cyclic; compounds of this kind are considered in the following section.

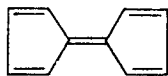
XIII. AROMATICITY

Some cyclic conjugated systems are much more stable than open-chain analogues while others are not; compounds of the former type are termed aromatic. This extra stabilization naturally has a profound effect on chemical reactivity and it is therefore very important that we should have some way of predicting the degree of aromatic stabilization in given systems.

The only satisfactory approach to this problem at present involves the use of perturbational methods. Attempts to calculate resonance energies indirectly, by comparing calculated total energies of a compound with that of a single classical structure for it, have proved ineffective. Thus calculations of this kind have failed to account for the special stability of monocyclic compounds containing $4n + 2$ electrons (Hückel's rule), and they predict that all the compounds XVII–XXIII should be aromatic whereas the only one that is aromatic is azulene (XXII).



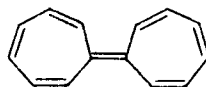
(XVII)



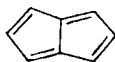
(XVIII)



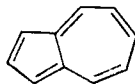
(XIX)



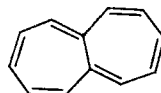
(XX)



(XXI)



(XXII)



(XXIII)

The π energy of a non-classical conjugated hydrocarbon can be compared directly with that of a classical analogue by the PMO method.¹⁴ Consider an even monocyclic polyene. This can be formed by fusion of methyl with an odd AH with one atom less. These components can also be fused to form an acyclic polyene. Comparison gives the *aromatic energy* of the cyclic system by difference. In this way we find that rings with $4n + 2$ atoms are more stable, and those with $4n$ atoms less stable, than analogous acyclic compounds. The same method can be used for the bicyclic systems XVII, XIX, XXI, XXII, XXIII. The procedure is indicated below

(1) Compounds derived from methyl + pentadienate:



(NBMO coefficients $a = 1/\sqrt{3}$).



$$\delta E_{\pi} = 2a\beta$$

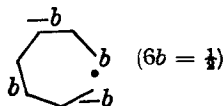


$$\delta E_{\pi} = 2a\beta$$

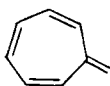


$$\delta E_{\pi} = 2\beta(a + a) = 4a\beta$$

(2) Compounds derived from methyl + heptatrienate:



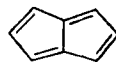
$$\delta E_{\pi} = 2b\beta$$



$$\delta E_{\pi} = 2b\beta$$

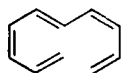
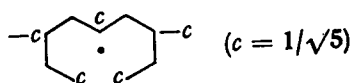


$$\delta E_{\pi} = 2\beta(b - b) = 0$$

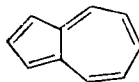
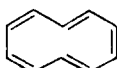
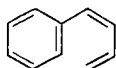


Hence heptafulvene is non-aromatic but cyclooctatetraene and pentalene (XXI) are *antiaromatic* (aromatic energy $-2b\beta$).

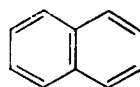
(3) Compounds derived from methyl + nonatetraenate:



$$\delta E_{\pi} = 2c\beta$$



in each case $\delta E_{\pi} = 4c\beta$



$$\delta E_{\pi} = 6c\beta$$

Hence phenylbutadiene, cyclodecapentiene, and azulene (XXII) are aromatic (aromatic energy $2c\beta$) while naphthalene is not only aromatic but has twice as large an aromatic energy ($4c\beta$). Naphthalene can be regarded as a bicyclic aromatic system, but azulene is really monocyclic; the central bond should contribute little to its stability and should be essentially simple, its only function being to enable the cyclodecapentaene ring to exist in a planar form. (X-ray studies⁴⁹ have shown that the central bond in azulene is very long.)

These arguments can of course be extended to heterocyclic systems by using the perturbation methods introduced by Longuet-Higgins (Section IX above). In general a heterocyclic system will be aromatic if and only if the isoconjugate hydrocarbon is aromatic. A similar perturbation treatment can also be used to show that odd monocyclic systems should be most stable if they contain $4n + 2$ electrons; this of course completes the derivation of Hückel's rule.

XIV. INDIRECT CALCULATIONS OF δE_{π}

It is of course possible to calculate δE_{π} indirectly by difference from the delocalization energies of the reactants and of the products or transition state. Indeed most of the reported calculations have made use of this procedure, the π energies usually being estimated by using the Hückel method. The trouble with this approach is that the assumptions underlying the Hückel method break down for compounds other than AH's, while in the case of AH's the PMO method is not only much simpler but also more

accurate.¹³ As Eq. (33) shows, one cannot assume the parameter α_i in the Hückel treatment to be a constant, characteristic of atom i and independent of the rest of the molecule, unless $q_i = 1$ at each position; this is so only in an AH. Therefore although the Hückel method may prove satisfactory in the case of non-alternant compounds and compounds containing heteroatoms, it cannot be used in such cases with any confidence and it often fails badly.

A typical failure of the Hückel method in the case of non-alternant systems is its prediction that all the hydrocarbons XVII–XXIII should be aromatic; of these only azulene (XXII) shows aromatic properties.

A similar failure in the case of heterocyclic compounds is shown by the basicity of even heteroaromatic bases such as pyridine or quinoline. These all have similar basic strengths, as the simple PMO method predicts (Section IX). However the charge densities on the nitrogen atoms calculated⁵¹ by the Hückel method are not the same (Table IV); application of Eq. (101) would then imply that the bases should differ considerably in strength.

TABLE IV. Calculations for Heteroaromatic Bases

Compound	pK_A	q_n calculated by:		ΔE_n , eV
		Hückel method	Pople method	calculated by: Pariser–Parr method
Pyridine	5.23	1.079	1.090	–14.42
Quinoline	4.94	1.088	1.092	–15.06
Isoquinidine	5.33	1.081	1.090	–15.22
Acridine	5.60	1.104	1.099	–15.81

In spite of these shortcomings the Hückel method has proved very successful in interpreting the chemistry of systems where the PMO method cannot easily be applied; some examples are given in the following section. Applications of this kind should of course be made with great care. They should be regarded as an aid in determining structures and reaction mechanisms rather than as an absolute guide.

It would naturally be better if more accurate MO approximations could be used in such cases and a number of calculations have already been reported using the Pariser–Parr and SCF methods. Of these the SCF methods are clearly preferable for the present purpose since they give ground state wave functions in the form of single determinants; the Pariser–Parr method was designed primarily to account for light absorption, and here configuration interaction must be introduced since excited states are involved. Any SCF method automatically gives a ground state function which interacts only with doubly or more highly excited states; this is clearly much more convenient than a ground state function expressed as a combination of Slater determinants.

There are two main difficulties in applying the SCF treatment to chemical problems. First, one can only achieve sufficient accuracy if one is prepared to regard the integrals appearing in it as parameters; much work will be needed to establish the best values of these to use. Secondly, serious difficulties arise in calculating δE_π by difference from the π energies of dissimilar conjugated systems; it is not at all clear how the core potentials should be treated in cases where one is comparing anisoconjugate systems with dissimilar cores.

Two examples will illustrate these points. The first is provided by the problem of estimating the basicity of simple heteroaromatic bases. As we have seen (Table IV), the Hückel method fails to predict that the basicity should be the same in different bases of this type. Daudel and his collaborators⁵¹ have used the Pariser–Parr method to estimate the difference in π energy between the bases and their conjugated acids; the values they obtained, shown in the last column of Table IV, would imply an enormous change in basic strength along the series. They tried to get around this difficulty by supposing that the changes in π energy are almost exactly counterbalanced by opposite changes in solvation energy of the ions; however, such a coincidence seems unlikely. We have calculated the π -electron densities on nitrogen in these bases by the Pople method, using Pariser–Parr electron repulsion integrals and theoretical values for the other parameters; the values, shown in the fourth column of Table IV, also fail to predict that the bases should be similar in strength, although the change in q_n is less along the series than it is for the Hückel method, and

although the variation is less than that given by the Pariser–Parr treatment.

The second problem is the prediction of the orientation of electrophilic substitution in 10,9-borazarophenanthrene. In order to estimate this one must compare the total energies of two systems that differ in the number of conjugated atoms. Two difficulties arise when one tries to do this by the Pople method. First, it is probably no longer justifiable to neglect penetration integrals if one wants to know the relative energies of two anisoconjugate systems to a high degree of accuracy. Secondly, it is difficult to know how best to compute the core repulsion. These uncertainties are probably responsible for the unsatisfactory results given by the Pople method in this case. Figure 6 shows localization energies for electrophilic substitution calculated by Dr. Joyce J. Kaufman.⁵² These correctly predict that the 8-position should be the most reactive; however they predict that the 6-position should be much less reactive than the 8-position, which is incorrect, and that the 7-position should be the third most reactive, which is probably also incorrect. Here the simple PMO method seems to be much superior (Fig. 5a).

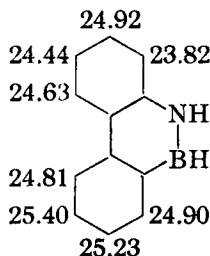


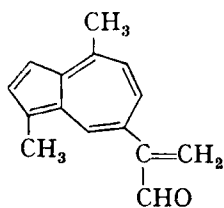
Fig. 6. Localization energies (eV) calculated for 10,9-borazarophenanthrene⁵² by the Pople method.

We have obtained very similar results in treating borazarophenanthrene by the Pople method and we have found similar vagaries in the localization energies given by it for other heteroaromatic compounds. The variations in the energies are too large, and the method, as used by us, also fails to predict correctly the relative reactivities of different ring systems. More work needs to be done to overcome these difficulties before the SCF method can be used to treat problems of this kind.

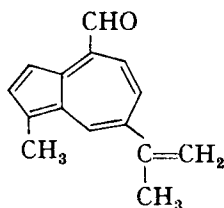
A much more promising way of using the SCF method seems to be to apply perturbation theory to it. Pople⁵³ has published the necessary equations for treating various problems in this way; the differences from the simple Hückel PMO method are relatively small.

We may conclude by giving some examples of chemical problems where the indirect calculation of reactivity has given new and useful information. These examples show that quantum chemistry, even in its present primitive form, has already become an important tool for helping to determine structures and reaction mechanisms.

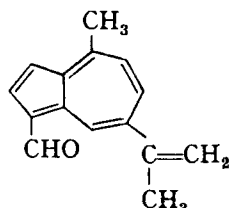
(1) Lactaroviolin is a naturally occurring azulene derivative with interesting pharmacological properties. Chemical degradation quickly established it to have one of the three structures XXIV, XXV, or XXVI, but it was difficult to distinguish between these by chemical methods. Heilbronner⁵⁴ solved this problem by comparing the physical properties of lactaroviolin with those calculated for each of the three structures by the Hückel method; in this way he showed that structure XXVI must be correct. In this case the use of the Hückel method was justified by the fact that it had given successful predictions for a number of analogous azulene derivatives of known structure.



(XXIV)



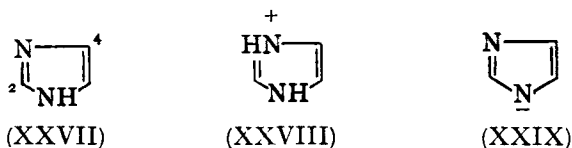
(XXV)



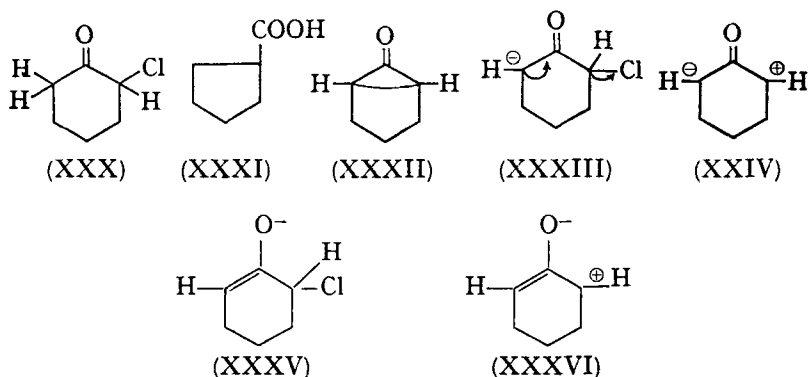
(XXVI)

(2) Imidazole (XXVII) couples with diazonium salts in the 2-position, although it normally undergoes electrophilic substitution in the 4-position. One possible explanation might be that under acid conditions it is the conjugate acid (XXVIII) that undergoes substitution; but Brown and his collaborators⁵⁵ found that MO calculations predicted both XXVII and XXVIII to react preferentially in the 4-position. The calculations suggested, however, that the conjugate base XXIX would react preferentially

in the 2-position, unlike XXVII or XXVIII; experiment showed that the diazocoupling reaction does in fact involve attack by the diazonium ion on the conjugate base XXIX, rather than on imidazole itself.



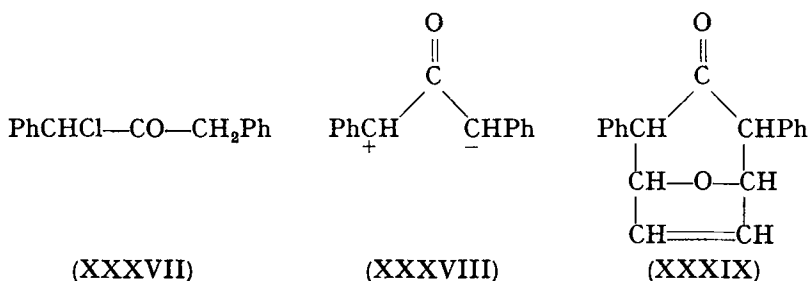
(3) In the Favorskii reaction a haloketone reacts with alkali to give a carboxylic acid with simultaneous skeletal rearrangement; thus 2-chlorocyclohexanone (XXX) gives cyclopentanecarboxylic acid (XXXI)



A very plausible mechanism for this would involve loss of hydrogen chloride from XXII to form the bicyclohexanone (XXXII); this is a cyclopropanone derivation and would certainly react at once with alkali to give XXXI. The problem is to explain how this comes about. One possibility might be α -elimination of HCl from XXX to form a carbene but this seems unlikely; such a carbene would in any case be expected to rearrange to cyclohexenone rather than to XXXII. Another possibility would be an internal displacement of chloride ion from the conjugate base of XXX, as indicated in XXXIII; this, however, is sterically improbable since in the grouping $-\text{CH}_2-\text{CH}^--\text{CO}-\text{CHCl}-$ the

four carbon atoms and the oxygen must lie in a plane, and the negatively charged carbon has its extra electrons in a *p*-orbital whose node lies in this plane. Burr and Dewar⁵⁶ suggested that XXXIII might ionize directly to a mesomeric intermediate for which various dipolar resonance structures can be written, e.g. XXXIV; they based this idea on Hückel calculations which indicated that XXXIV should have a much larger delocalization energy than XXXIII. The intermediate XXXIV once formed can collapse to XXXII. This mechanism can be put in a more intuitive form if one considers that the very electronegative oxygen atom will acquire more than its fair share of negative charge in XXXIII and XXXIV; if XXXIII approximates in structure to the enolate XXXV, and if XXXIV approximates to XXXVI, the reaction of XXXV to form XXXVI is seen to be the S_N1 ionization of an allyl chloride. Allyl chlorides of course undergo reactions of this kind very readily since the product is a mesomeric allyl cation, and here the reaction will be further assisted by the presence of a negatively charged substituent ($-O^-$).

This mechanism has recently been confirmed in a very beautiful way by Fort⁵⁷ who trapped the mesoionic intermediate XXXVIII formed from 1,3-diphenyl-1-chloropentane-2-one (XXXVII) with 2,6-collidine by carrying out the reaction in presence of furan; the adduct XXXIX was isolated, having been formed from XXXVIII and furan by a dipolar addition reaction.



(4) The possible existence of π -complex isomers of carbonium ions as stable reaction intermediates was predicted⁵⁸ on the basis of simple MO calculations before their existence had been demonstrated unambiguously. Intermediates of this kind are now recognized to play a very important role and their prediction

remains a striking contribution of MO theory to organic chemistry.

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References

1. Cf. Pitzer, K. S., *Ind. Eng. Chem.* **36**, 829 (1944).
2. Hammett, L. P., *Physical Organic Chemistry*, McGraw-Hill, New York, 1940.
3. Dewar, M. J. S., and Sampson, R. J., *J. Chem. Soc.* 2789 (1956).
4. See Olah, G. A., Pavlath, A. E., and Olah, J. A., *J. Am. Chem. Soc.* **80**, 6540 (1958) and references cited there.
5. Dewar, M. J. S., and Schmeising, H. N., *Tetrahedron* **5**, 166 (1959); **11**, 96 (1960).
6. Wheland, G. W., *J. Am. Chem. Soc.* **64**, 900 (1942).
7. Pullman, B., and Pullman, A., *Les Théories Electroniques de la Chimie Organique*, Masson et Cie., Paris, 1952; Daudel, R., Lefebvre, R., and Moser, C., *Quantum Chemistry*, Interscience, New York, 1959.
8. Pople, J. A., *Trans. Faraday Soc.* **49**, 1375 (1953).
9. Coulson, C. A., and Rushbrook, G. S., *Proc. Cambridge Phil. Soc.* **36**, 193 (1940).
10. See Pople, J. A., *J. Phys. Chem.* **61**, 6 (1957).
11. Moffitt, W. E., *Trans. Faraday Soc.* **45**, 373 (1949).
12. The definition of free valence was originally given in terms of bond orders defined by resonance theory; for a general account see ref. 7.
13. Streitwieser, A., *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961.
14. Dewar, M. J. S., *J. Am. Chem. Soc.* **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).
15. Longuet-Higgins, H. C., *J. Chem. Phys.* **18**, 265, 275, 283 (1950).
16. Dewar, M. J. S., *Sci. Progr. (London)* **40**, 604 (1952); *Prog. Org. Chem.* **2**, 1 (1953); *Ann. Rep. Chem. Soc.* **53**, 126 (1956).
17. Dewar, M. J. S., Mole, T., and Warford, E. W. T., *J. Chem. Soc.* 3581 (1956); Dewar, M. J. S., and Mole, T., *ibid.* 342 (1957).
18. Dewar, M. J. S., and Longuet-Higgins, H. C., *Proc. Roy. Soc. (London)* **A214**, 482 (1952).
19. Coulson, C. A., and Longuet-Higgins, H. C., *Proc. Roy. Soc. (London)* **A191**, 39 (1947); **A192**, 16 (1947); **A193**, 447, 456 (1948); **A195**, 188 (1948).
20. See Williams, G. H., *Homolytic Aromatic Substitution*, Pergamon, Oxford, 1960.
21. Dewar, M. J. S., and Maitlis, P. M., *J. Chem. Soc.* 944, 2518, 2521 (1957).
22. Dewar, M. J. S., and Warford, E. W. T., *J. Chem. Soc.* 3570 (1956).
23. Dewar, M. J. S., and Kubba, V. P., *Tetrahedron* **7**, 213 (1959).

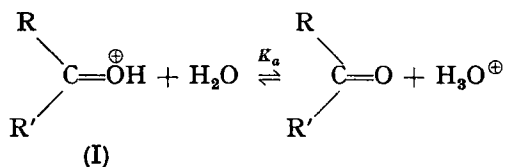
24. Culbertson, G., and Pettit, R., *J. Am. Chem. Soc.* **86**, 741 (1963).
25. Olah, G. A., and Kuhn, S. J., *J. Am. Chem. Soc.* **80**, 6535 (1958); J. F. Bunnett, *Quart. Rev. Chem. Soc.* **12**, 1 (1958).
26. See Melander, L., *Isotope Effects on Reaction Rates*, Ronald Press Co., New York, 1960.
27. See Bell, R. P., *Acid Base Catalysis*, Clarendon Press, Oxford, 1941, p. 168, and reference cited there.
28. Brown, H. C., and Nelson, K. L., *J. Am. Chem. Soc.* **75**, 6292 (1953).
29. Dewar, M. J. S., and Sampson, R. J., *J. Chem. Soc.* 2946 (1957) and references cited there.
30. Winstein, S., Grunwald, E., and Jones, H. W., *J. Am. Chem. Soc.* **73**, 2300 (1951).
31. Swain, C. G., and Langsdorf, W. P., *J. Am. Chem. Soc.* **73**, 2813 (1951).
32. Doering, W. E., and Zeiss, H. H., *J. Am. Chem. Soc.* **75**, 4733 (1953).
33. See Streitwieser, A., *Chem. Rev.*, **59**, 573 (1956).
34. Pullman, A., Pullman, B., and Nakajima, T., *Bull. Soc. Chim. France* 590, 594, 663 (1959).
35. Bunel, S., Chalvet, O., Daudel, R., Nesbet, R., and Peradejordi, F., *Compt. Rend.* **252**, 2890 (1961).
36. Hammett, L. P., *Chem. Rev.* **17**, 125 (1935); see McDaniel, D. H., and Brown, H. C., *Chem. Rev.* **23**, 420 (1958).
37. van Bekkum, H., Verkade, P. E., and Wepster, B. M., *Rec. Trav. Chim.* **78**, 815 (1959).
38. Dewar, M. J. S., and Grisdale, P. J., *J. Am. Chem. Soc.* **84**, 3548 (1962).
39. Ri, T., and Eyring, H., *J. Chem. Phys.* **8**, 433 (1940).
40. Dewar, M. J. S., *Discussions Faraday Soc.* **2**, 261 (1947).
41. Kornblum, N., Smiley, R. A., Blackwood, R. K., and Iffland, D. C., *J. Am. Chem. Soc.* **77**, 6269 (1955).
42. Doering, W. E., personal communication.
43. Fukui, K., Yonezawa, T., and Shingu, H., *J. Chem. Phys.* **20**, 722 (1952); Fukui, K., Yonezawa, T., and Nagata, C., *ibid.* **27**, 1247 (1957); **31**, 350 (1959).
44. For a recent paper and references see Dewar, M. J. S., Kaneko, C., and Bhattachargee, M. K., *J. Am. Chem. Soc.* **84**, 4884 (1962).
45. Evans, M. G., and Warhurst, E., *Trans. Faraday Soc.* **34**, 614 (1938); **35**, 824 (1939).
46. See Berson, J. A., and Remanick, A., *J. Am. Chem. Soc.* **83**, 4947 (1961) and references cited there.
47. Brown, R. D., *J. Chem. Soc.* 1950, 3129 (1951).
48. Dewar, M. J. S., *Hyperconjugation*, Ronald Press Co., New York, 1962.
49. Dewar, M. J. S., *Proc. Cambridge Phil. Soc.* **45**, 639 (1949).
50. Robertson, J. M., Shearer, H. M. M., Sim, G. A., and Watson, D. G., *Acta Cryst.* **15**, 1 (1962).
51. Daudel, R. *et al.*, *Compt. Rend.* **252**, 2890 (1961).

52. Kaufman, J. J., *Symposium on Boron-Nitrogen Chemistry*, Durham, North Carolina, 1963.
53. Pople, J. A., *Proc. Roy. Soc. (London)* **A233**, 233 (1955).
54. Heilbronner, E., and Schmid, R. W., *Helv. Chim. Acta* **37**, 2018 (1954).
55. See Brown, R. D., Duffin, H. C., Maynard, J. C., and Ridd, J. H., *J. Chem. Soc.* 3937 (1953).
56. Burr, J. G., and Dewar, M. J. S., *J. Chem. Soc.*, 1201 (1954).
57. Fort, A. W., *J. Am. Chem. Soc.* **84**, 4979 (1962).
58. Cf. Dewar, M. J. S., *The Electronic Theory of Organic Chemistry*, Clarendon Press, Oxford, 1949; *Bull. Soc. Chim. France* **18**, c71 (1951).

A SELF-CONSISTENT FIELD MOLECULAR ORBITAL TREATMENT OF CARBONYL BASE STRENGTH

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The ease with which the carbonyl group of an organic aldehyde or ketone accepts a proton to give the oxonium salt (I) can be of considerable importance from the viewpoint of structural and mechanistic theory. Despite the now classical studies of Hammett and his school,¹ extensive pK_a data for equilibria of the type



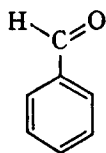
have become available only in the past few years, principally through the work of Campbell and Edward² in the aliphatic series and of Stewart and his group³ in the aromatic series. The data of these and other investigators suggest that the free energy change upon protonation of a carbonyl compound, as for any basic species, is the resultant of several energy terms, including inductive and hybridization effects, steric repulsion terms, solvation energies and a π -energy term.⁴ If we restrict ourselves to planar, unsaturated carbonyl systems lacking major steric or polar effects, then the pK_a of a carbonyl conjugate acid (I) should depend to a considerable extent upon the π -energy difference between the neutral and protonated carbonyl species.

Early in 1963 Culbertson and Pettit⁵ reported the base strengths of ten simple polycyclic benzenoid aldehydes and ketones and attempted to relate the pK_a values to molecular structure. They were able to show the existence of a linear correlation between pK_a and the *protonation π energy*, that is, the gain in π energy of the protonated over the neutral compound. In their treatment

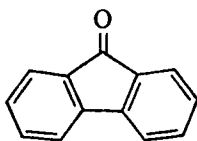
this energy difference was calculated by a perturbation approximation based on the Hückel molecular orbital theory of alternant conjugated systems. While this approach has the virtue of simplicity and appears to extend to simple olefinic ketones,⁶ it is in principle invalid for the large and important class of carbonyl bases which possess a non-alternant π -electron system.

Non-alternant ketones such as tropone⁷ and diphenylcyclopropanone⁸ are of theoretical interest in that their high basicities have been taken to indicate aromatic stabilization in the corresponding conjugate acids. If the σ bond, steric and solvation terms for the protonation of non-alternants do not differ greatly from those of alternant compounds it should be possible to correlate non-alternant carbonyl pK_a values with protonation π energies provided that these π energies can be properly evaluated. As a first step, one can calculate the Hückel molecular orbitals using a suitable model for the neutral and protonated form of each species of interest.⁹ It is generally recognized, however, that the independent electron assumption of the simple Hückel approach often fails in predicting the structure and reactivity of non-alternant molecules. This failure arises in large measure from neglect of repulsion terms which represent the interaction energy of each electron with the other electrons of the π system.

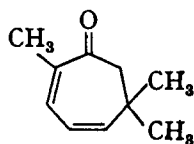
Representative carbonyl bases



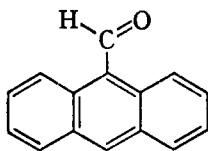
Benzaldehyde



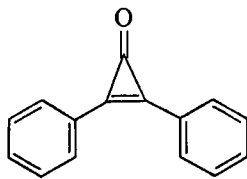
Fluorenone



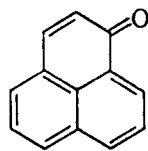
Eucarvone



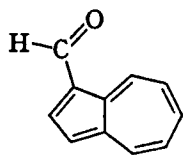
9-Anthraldehyde



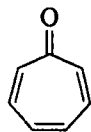
Diphenylcyclopropanone



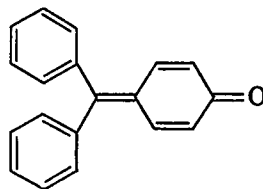
Perinaphthenone



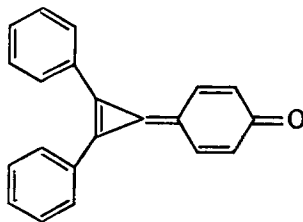
Azulene-1-aldehyde



Tropone



Fuchsonone



Diphenylquinocyclopropene

At a second level of approximation, therefore, one can introduce electron repulsion through use of a Pople-type matrix¹⁰ in an iterative procedure.

The initial Hückel calculations can be employed to obtain preliminary values for the electron densities and bond orders, from which the self-consistent field matrix elements can be evaluated by introduction of the chosen core potentials and electron repulsion integrals.¹¹ Table I lists the ionization potentials, electron affinities and nuclear charges employed in the present calculations.

TABLE I. Pariser-Parr-Pople Parameters

	Ion. pot., eV	El. affin., eV	Eff. nuclear charge Z	β_{C-X}^{core} , eV	r_{C-X} , Å
Neutral species					
C	11.22	0.69	3.25	-2.39	1.40
O	17.17	2.97	4.55	-3.00	1.22
Protonated species					
C	11.22	0.69	3.25	-2.39	1.40
O	35.50	13.95	4.90	-2.12	1.38

Ten unsaturated carbonyl compounds representing a variety of structural types were selected for study. These are given in Table II, together with their pK_a values and dipole moments, where available; the non-alternant systems are indicated in italics. The fourth column contains the π dipole moments of the neutral molecules as obtained by the Pariser–Parr–Pople method using the parameters of Table I.

TABLE II. Representative Carbonyl Systems

Compound	pK_a	μ_{exptl}^{15}	μ_{calcd}
1. Benzaldehyde	-6.99 ⁵	2.76 ^D	2.86 ^D
2. <i>Fluorenone</i>	-6.65 ³	3.35	2.96
3. Eucarvone	-4.9 ⁶		3.35
4. 9-Anthraldehyde	-4.81 ⁵		3.13
5. <i>Diphenylcyclopropenone</i>	-3.2 ¹²	5.08 ¹⁶	5.14
6. Perinaphthenone	-1.40 ⁵	4.2 ¹²	4.23
7. <i>Azulene-1-aldehyde</i>	-1.0 ¹²		4.10
8. <i>Tropone</i>	-0.6 ¹²	4.3	4.51
9. Fuchsone	1.7 ¹³		6.69
10. <i>Diphenylquinocyclopropene</i>	5 ¹⁴		13.16

Figure 1 depicts the plot of pK_a against Hückel protonation energies. This plot has an average deviation of 1.24 pK units, and it is significant that the non-alternants tropone, azulene-1-aldehyde and diphenylcyclopropenone each deviate more than 2 pK units from the correlation line. The plot of pK_a against Pariser–Parr–Pople protonation energies yields the improved correlation in Fig. 2 with an average deviation of 0.90 pK units; the improvement for the non-alternants is appreciable. The slope of the correlation line in Fig. 2 gives the linear relation

$$pK_a = 3.64E - 78.72$$

where E is the Pariser–Parr–Pople protonation π energy in electron volts.

It is not clear from this preliminary study whether the deviations of Fig. 2 arise from an improper evaluation of π energies, or from terms independent of the structure of the π system. The calculation

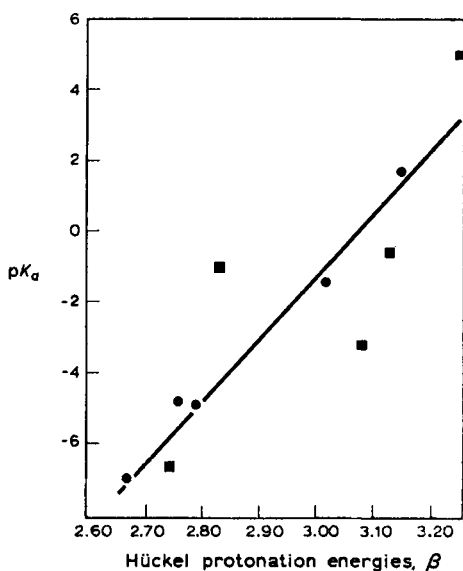


Fig. 1. Correlation of pK_a with Hückel protonation energy. Circles and squares denote alternant and non-alternant systems, respectively.

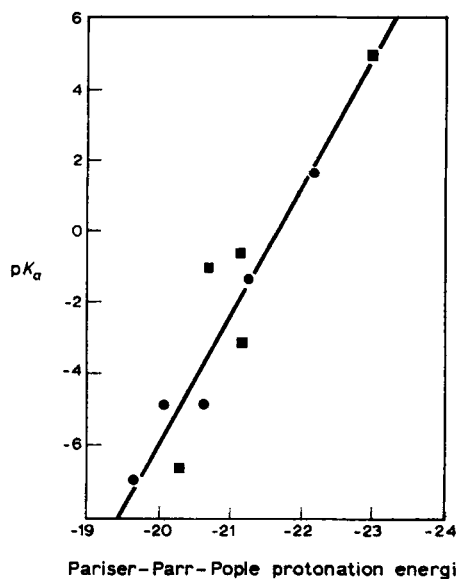


Fig. 2. Correlation of pK_a with Pariser-Parr-Pople protonation energy. Circles and squares denote alternant and non-alternant systems, respectively.

of further carbonyl systems, both carbocyclic and heterocyclic, is now in progress to help evaluate the scope and limitations of the present approach.

Acknowledgment

The author is deeply indebted to Professor Raymond Daudel for his kind hospitality during the summers of 1962 and 1963 at the Centre de Mécanique Ondulatoire Appliquée (Paris 19, France) where the bulk of this study was carried out. He is especially grateful to Dr. Odilon Chalvet for invaluable advice and patient guidance throughout the course of this work, and would like to thank Dr. Joyce Kaufman and Professor Hans Jaffé for several stimulating discussions.

References

1. Flexser, L. A., Hammett, L. P., and Dingwall, A., *J. Am. Chem. Soc.* **57**, 2103 (1935); Flexser, L. A., and Hammett, L. P., *ibid.* **60**, 885 (1938); Zucker, L., and Hammett, L. P., *ibid.* **61**, 2779-2798 (1939).
2. Campbell, H. J., and Edward, J. T., *Can. J. Chem.* **38**, 2109 (1960).
3. Stewart, R., and Yates, K., *J. Am. Chem. Soc.* **80**, 6355 (1958); *Can. J. Chem.* **37**, 664 (1959); Stewart, R., Granger, M., Moodie, R., and Muenster, L., *ibid.* **41**, 1065 (1963).
4. A precise treatment of the free energy change of protonation, expressed in terms of the partition functions and the various energy components, can be found in a discussion of the basic strengths of nitrogen heterocycles by Chalvet, O., Daudel, R., and Peradejordi, F., *J. Chim. Phys.* **59**, 709 (1962). In their treatment, as in the present case, possible effects due to relative differences in molecular partition functions are neglected.
5. Culbertson, G., and Pettit, R., *J. Am. Chem. Soc.* **85**, 741 (1963).
6. Holmes, J. D., and Pettit, R., *J. Am. Chem. Soc.* **85**, 2531 (1963).
7. Dauben, H. J., and Ringold, H. J., *J. Am. Chem. Soc.* **73**, 876 (1951); von E. Doering, W., and Detert, F. L., *ibid.* **73**, 876 (1951).
8. Breslow, R., Haynie, R., and Mirra, J., *J. Am. Chem. Soc.* **81**, 247 (1959); Volpin, M. E., Koreshkov, Y. D., and Kursanov, D. N., *Izvest. Akad. Nauk. S.S.S.R. (Otdel. Khim. Nauk.)*, **1959**, 560.
9. The Hückel parameters for the neutral forms were chosen as $\alpha_O = \alpha_C + \beta$, $\beta_{C-O} = 1.40\beta_{C-C}$; for the protonated forms, $\alpha_O = \alpha_C + 3\beta$, $\beta_{C-O} = 0.80\beta_{C-C}$. These values were in reasonable agreement with those found from the subsequent Pariser-Parr-Pople treatment, taking the benzenoid values $\alpha_C = -5.95$ and $\beta_{CC} = -4.815$ eV.

10. Leading references to the self-consistent field method employed here are cited by Pople, J. A., *J. Phys. Chem.* **61**, 6 (1957). Calculations of the Hückel and SCF orbitals were executed on an IBM-7090 computer using an entirely automatic program written by Dr. Bessis of the Centre de Mécanique Ondulatoire Appliquée, Paris, France.
11. The two-center electron repulsion integrals are taken proportional to the interaction energy of unit point charges; cf. however, Pariser, R., and Parr, R. G., *J. Chem. Phys.* **21**, 767 (1953).
12. The pK_a values given for diphenylcyclopropenone, tropone and azulene-1-aldehyde were obtained by spectrophotometric titration with aqueous acids in the author's laboratory; these figures are accurate to ± 0.3 pK units. The dipole moment of perinaphthenone in benzene was measured by R. J. Best and K. Mead of the Stamford laboratories of the American Cyanamid Co., Connecticut, U.S.A.
13. Kende, A., *J. Am. Chem. Soc.* **85**, 1882 (1963). Since the pK_a determinations of fuchson and 2,6-dibromo-8,9-diphenylquinocyclopropene were of necessity carried out in a nonaqueous solvent, the value for the hypothetical "aqueous" pK_a could easily differ ± 0.5 pK units from that given in Table II.
14. By extrapolation from the nonaqueous pK_a 3.8 obtained,¹ for the 2,6-dibromo substitution product.
15. Except where otherwise noted, these moments were taken from Hückel, W., *Theoretical Principles of Organic Chemistry*, Elsevier, Amsterdam, 1958, Chapter XII.
16. Kursanov, D., Volpin, M., and Kōreshkov, Y., *Z. Obsch. Khim.* **30**, 2877 (1960); *J. Gen. Chem. U.S.S.R. (Eng. Transl.)* **30**, 2855 (1960).

CHEMISORPTION OF ETHYLENE ON METALS AND CATALYTIC HYDROGENATION

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I. PREVIOUS WORK

The problem of adsorption was first treated by Lenel in 1933.³ Lennard-Jones, Strachan, Devonshire and Goodwin^{1a-g} followed, between 1935 and 1937, with a series of papers of a theoretical nature. During this period contributions were also made by Barrer,⁴ Goodwin⁵ and Orr.⁶ Since that time the problem has been re-examined by Crawford and Tomkins⁷ and by Rhodin⁸ during 1948 and 1949.

Chemisorption has been studied by various methods. Grimley,⁹ Koutecky¹⁰⁻¹² and Syrkin¹³ have all used the molecular orbital method; Volkenstein,¹⁴⁻¹⁶ the tight-binding method; Bontsch Brujevitch,^{17,18} the method of effective mass; Sherman, Eyring^{19,20} and Brenner,²¹ a localized model; and Koutecky,^{22,23} a two-dimensional crystal; the names of Eley,²⁵ Stevenson²⁶ and Koutecky^{27,28} may also be mentioned in connection with a general theory of the localized model.

Systematic studies of catalysis have been made not only on the basis of thermodynamic theory, but also on the basis of a textural theory, that is consideration of active centres (Eyring³⁰), while others have been based upon a localized model. The earliest publications are those of Coulson and Longuet-Higgins³², who used the method of molecular orbitals, and Daudel and Sandorfy,³³ who used the method of mesomery, and the synthesis of the two methods by Sandorfy.³⁴ Among recent papers is that of Grimley³⁵ and also that of Volkenstein³⁶ and his predecessors,⁵²⁻⁷⁹ who used a semi-conductor model. Roguinskii⁷³ classified catalytic material into conductors and non-conductors while Volkenstein⁷⁴⁻⁷⁶ used the results of solid-state physics in order to obtain a quantitative expression for adsorption and for catalysis. Aigrain and Dugas,⁶⁴ followed by Weitz,⁷⁰ studied the variation of the heat of adsorption with the quantity adsorbed. Other workers³⁷⁻⁴² have carried out studies in fields related to catalysis.

II. GENERALITIES

In this paper, we propose to present a theoretical study of the catalytic hydrogenation of ethylene in order to compare the catalytic power of various transition metals. As a basic hypothesis, we have taken the fact that the ethylene molecule attaches itself to the metallic surface and this increases its reactivity. This is the same hypothesis as that of Coulson and Longuet-Higgins³² and Daudel and Sandorfy.³³ These workers calculated the variation of the index of free valence. We have considered it more interesting to endeavour to calculate the electronic potential barrier. We have used the system of reaction levels as shown in Fig. 1, where V is the potential barrier in the absence of catalyst, Q the heat of chemisorption, and U the potential barrier in passing

through the chemisorbed state. The chemical attack will be treated according to Wheland's approximation which treats the potential barrier in a rather schematic manner.

The calculation was carried out in the first stage with the usual approximations of the theory of conjugated molecules (Hückel

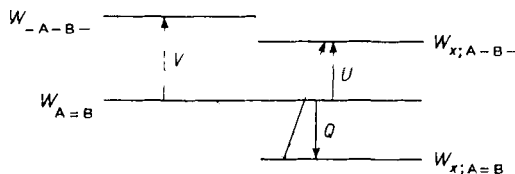


Fig. 1.

approximation), the discussion of which has been the subject of many papers. (See for example refs. 80 and 81.)

(1) For the ethylene molecule there is a σ energy and a π energy which are distinct and the σ energy remains the same in all cases in which it is used.

(2) The calculation of the π energy can be carried out by replacing it by a mono-electronic quantity in the Hamiltonian.

(3) The wave function results in the linear combination of the p_z functions of atoms A and B to which are added metal orbitals of the same symmetry. All the orbitals are considered to be orthogonal.

(4) The Hamiltonian is the same no matter what the nature of the atoms which take part in the structure considered.

$$\alpha = \int p_z^A \mathcal{H} p_z^B d\tau$$

$$\beta = \int p_z^A \mathcal{H} p_z^B d\tau$$

Under these conditions we write as usual

$$W_{-A-B-} = \sigma + 2\alpha$$

$$W_{A=B} = \sigma + 2\alpha + 2\beta$$

$$W_{A=B} - W_{-A-B-} = 2\beta$$

The calculation of other terms depends on numerous hypotheses which we will consider in later sections.

III. CONSTRUCTION OF THE MODEL

A. Hypotheses Concerning the Relative Positions of the Ethylene Molecule and That of the Metal

(1) The ethylene molecule has three symmetry axes. It may be supposed that one of these axes is perpendicular to the surface of the metal. In order to simplify the discussion we will consider only a cubic system. Under these conditions the symmetry axis may either fall on a row of atoms, in the middle of two rows (either in a cross or not), or in the middle of four rows. There are therefore twelve relative positions of the molecule and the lattice (assuming that the surface is perfect). These are shown in Fig. 2.

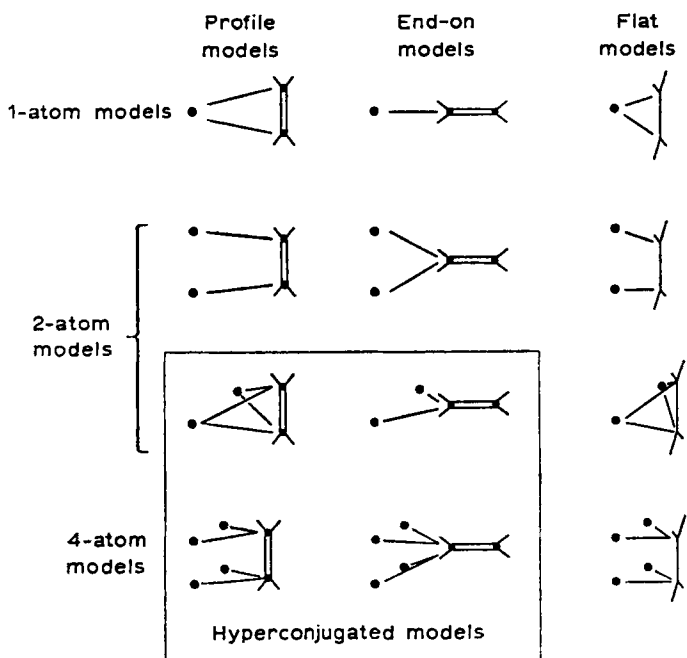


Fig. 2. Six other models have not been reproduced here. They correspond to the orientation possible with respect to the lattice diagonals.

The only change is in the distances of the rows.

(2) The second hypothesis concerns the distance of the carbon atom from the metallic atoms, which may be characterized by the corresponding value of the bond integrals.

B. Hypotheses Concerning the Geometric Structure of the Metal

(1) *Localized Model*

The metal is represented by the minimum number of atoms which allow the position of the molecule to be fixed. There are two justifications for this:

(1) Koutecky has shown that an atom-lattice bond may be localized with only the surface atom taking part in the bond.²⁹

(2) More simply, this model allows the introduction of two parameters representing on the one hand the electronegativity of the metal, and on the other hand the distance of the metal-carbon bond. These parameters may be considered as being semi-empirical and only of interest for comparing metals to each other.

(2) *Deep Chain Model*

The metal is represented by rows corresponding to the localized model. These rows are supposed to be of finite length. This permits us to obtain a symbolic representation of the size of the crystallites of the catalyst. This is an important physical factor.

(3) *Flat Lattice Model*

This allows us to represent the problem by supposing that we are dealing with a function which is antisymmetric with respect to the plane of the ethylene molecule. This is indeed the conclusion that we finally obtained. We suppose also that the planar lattice is finite and of varied form in order to study the influence of sites.

C. Hypotheses Concerning the Electronic Structure of the Metal

(1) *Introduction*

The "flat" model requires the introduction of an energy either of physical adsorption or of chemisorption by the formation of a σ bond. The other models require the introduction of the resonance of the π electrons. Thus we obtain a conjugated model if the metal atoms are in the plane of the ethylene molecule. We obtain

hyperconjugated models if the metal atoms are at one end or the other of the ethylene molecule. In this case, wave functions ψ_1 and ψ_2 can be replaced as indicated in Fig. 3 by the anti-symmetric combination $\psi_1 + \psi_2$ and the symmetric combination $\psi_1 - \psi_2$. We will consider two representations of the π electrons of the metal which we propose to designate p and d respectively.

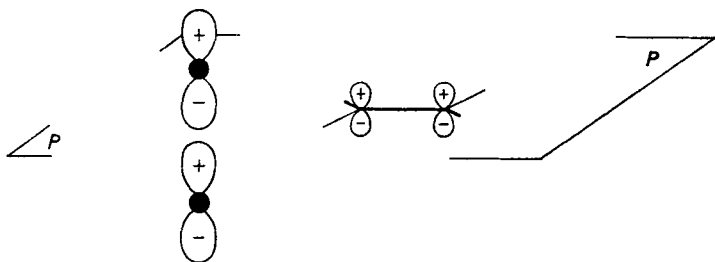


Fig. 3.

(2) Metal p

A ghost orbital p_z is imagined as being attached to each atom of the metal. This orbital represents that part of the wave function of the atom which is antisymmetric with respect to the plane of the ethylene molecule. It is supposed also that each atom contributes one electron.

One may consider a certain number of effective parameters in order to characterize the metal and its bond with the ethylene molecule. Considering only conjugated systems, we have introduced those shown in Fig. 4.

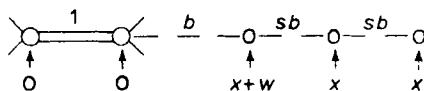


Fig. 4.

The unit β can be considered to be of the order of 27 kcal/mole; the parameter x is taken to have a value of the order of the electronegativity of the metal measured in β units compared with that of C, that is to say from 0 to -1 ; b is taken to be of the order of unity.

(3) *Metal d*

(a) *Principles.* In this model we have endeavoured to approach closer to the physical reality. We suppose that the valence electrons which are *s* electrons do not interact directly with the ethylene molecule. Each metallic ion is reduced to its *d* electrons.

The five *d* orbitals may be written :

$$\begin{aligned} 3d_z &\sim 2z^2 - x^2 - y^2 \\ 3d_{x+y} &\sim xz \\ 3d_{y+z} &\sim yz \\ 3d_{xy} &\sim x^2 - y^2 \\ 3d_{x-y} &\sim xy \end{aligned}$$

If we look for the resonance in the *x-y* plane we need only consider two: $3d_{x+z}$ and $3d_{y+z}$. Obviously the expressions which we have written here correspond to an arbitrary base and one may rotate the axes at will.

The number of electrons in the *d* shell varies from *n* = 0 for K to *n* = 10 for Zn. We suppose that each of the two orbitals $3d_{x+z}$ and $3d_{y+z}$ contain *n*/5 electrons. Under these conditions, almost all hypotheses concerning the nature of the bond between the metals are eliminated. This state of affairs can be corrected by introducing corrections to the value *n*. Since this model is relatively rarely encountered, we will give some examples.

(b) *Study of the carbon-metal bonds.* Consider the bond C-X. Writing *b*₁ and *b*₂ for the bond integrals in β units gives

$$\begin{aligned} x &= \frac{\alpha_x - \alpha}{\beta} \\ m &= \frac{\alpha - \varepsilon}{\beta} \end{aligned}$$

The secular determinant may be written

$$\Delta = (m + x)[m^2 + xm - (b_1^2 + b_2^2)]$$

*b*₁ and *b*₂ appearing only as *b*² = *b*₁² + *b*₂². This means that we may arbitrarily rotate the axes which define the orbitals. Under

these circumstances, Fig. 5 gives the correspondence between the levels of the metal p and the metal d .

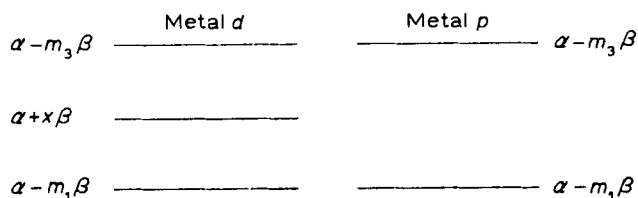


Fig. 5.

It will be observed that two electrons may be added on the level $\alpha + \beta x$, that is to say, five electrons to the metal without modifying the bond energy. This situation is very general. In all problems concerning the transition metals, we encounter degrees of filling of the levels. Figure 6 represents the variation of the bond energy with the progressive degree of filling of the d shell. Figures 7 and 8 represent the charges.

(c) *Study of the triangular model.* Figure 9 illustrates this model diagrammatically and shows the corresponding levels. The cal-

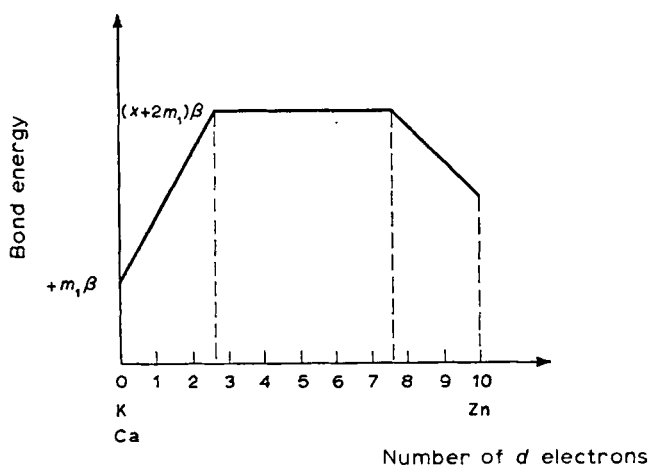


Fig. 6. Bond energy of the complex $C-X$ as a function of the number of electrons.

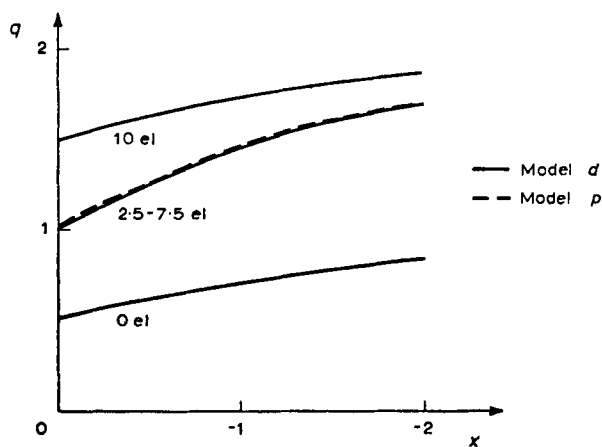


Fig. 7. Charge on C in the C-X complex as a function of x considering the number of electrons contributed by X and the model considered.

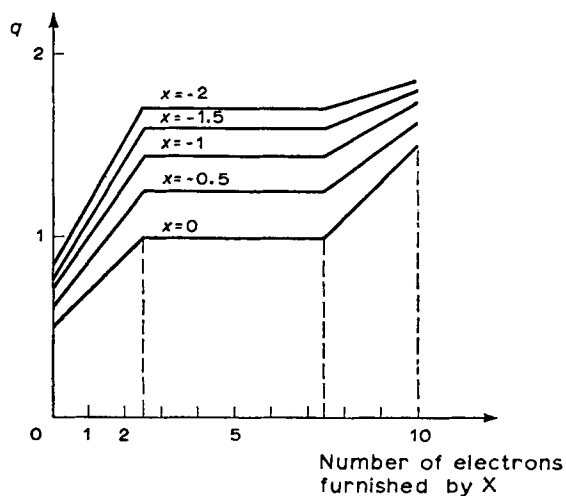


Fig. 8. Charge on C in C-X as a function of the number of electrons contributed by X considering x in the d model. The plateaus correspond to the values for the p model.

culuation of $Q = W_x + W_{AB} - W_x$; $_{AB}$ permits us to conclude that five electrons may be introduced without changing the bond energy. Figure 11 shows the general shape of the curves obtained

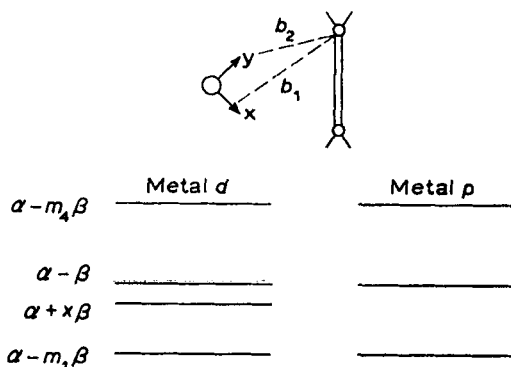
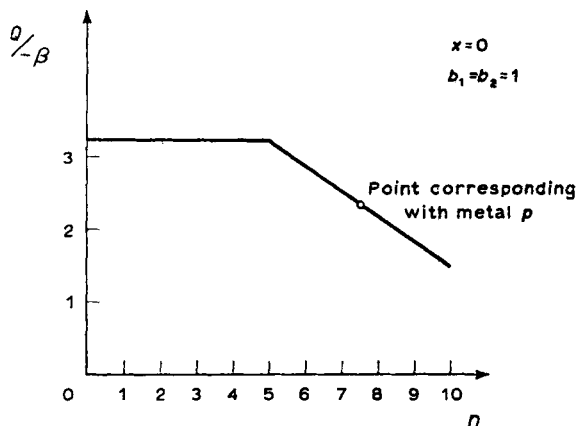


Fig. 9.

for the trapezoidal model, while Fig. 10 corresponds to the triangular model. It may be observed that there is a possibility of distinguishing clearly between these two models.

Fig. 10. Heat of chemisorption as a function of the number of *d* electrons.

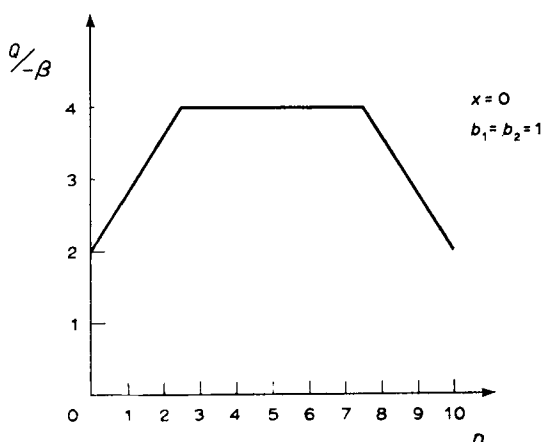


Fig. 11. Heat of chemisorption as a function of the number of d electrons. Trapezoidal model.

IV. RESULTS WHICH MAY BE OBTAINED BY CALCULATION AND CRITERIA TO BE CONSIDERED; ADJUSTMENT FOR EXPERIMENTAL VALUES

The following quantities may be adjusted in order to obtain agreement with their experimental values for the whole series of the transition metals:

- (1) the heat of chemisorption;
- (2) the potential barrier, U ;
- (3) the polarity of the film;
- (4) various observable quantities (the distance of the adsorbed film, alteration of the reticular distances within the metal, magnetic quantities).

The factors are: the nature of the metal, the size of the crystallite and the nature of the site.

It may be supposed that the appropriate model is the same for all the transition metals of the same row of the periodic table because of the similarities of these elements. It may only be necessary to eliminate the terms containing 0 or 1 d electrons for which the general properties are different.*

It is also possible to adjust the correlations to their experimental

* We thank Dr. Jørgensen for a discussion on this subject.

values, for example, $Q(U)$, because we have at our disposal the curve due to Beeck which gives the general shape without specifying units of U . These calculations were carried out on a desk calculator in the case of the localized models and that of the long-chain without chemisorption (Gouarne's method) and on an electronic machine (Institut Blaise Pascal) for the case of chain and lattice models.

Finally, in the case of chemisorption, an *a priori* criterion may be established which allows us to make predictions of a more theoretical nature: all other things being equal, the molecule situates itself in such a way that the energy of chemisorption is a maximum.

V. RESULTS

The planar model which introduces covalent bonds must be excluded. Within the limits of the separation of the π and σ energies, Fig. 12 gives the two possible curves, $Q(U)$. There are

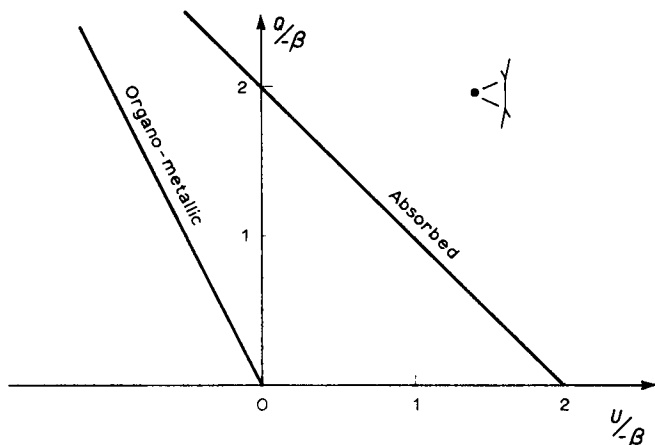


Fig. 12. Heat of chemisorption as a function of activation energy.

two possibilities. Either (1) there is simply physical adsorption, in which case the orders of magnitude are wrong (it is well known that the energies of physical adsorption are of the order of several calories/mole) or (2) there is a chemical bond and we never obtain an energy of activation.

The hyperconjugated models which bring into play resonance

with the two atoms of the metal must be excluded. When we apply the criterion of the strongest chemical adsorption it is known that the hyperconjugated models lead to an unstable equilibrium.

The "end on" conjugated models must be excluded. For $b \sim 1$, values of the heat of chemisorption are found which do not exceed 20 kcal/mole while the experimental values are between 20 and 100 kcal/mole, i.e. five times greater. Figures 13 and 14

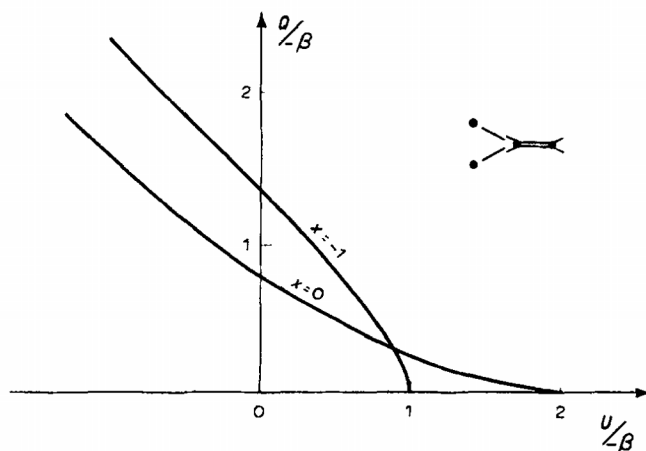


Fig. 13.

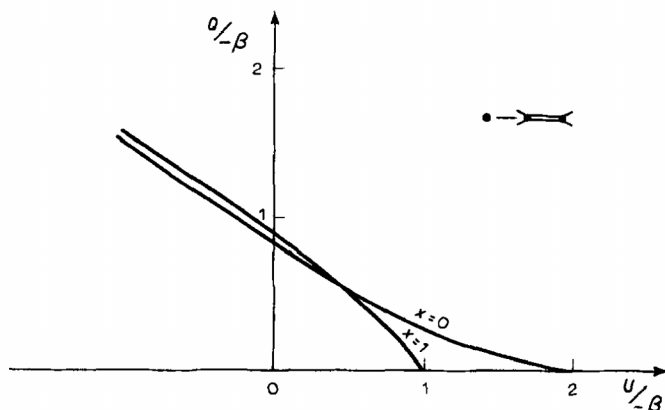


Fig. 14. Heat of chemisorption as a function of activation energy.

have been drawn for the metal p . If we apply, on the other hand, the criterion of the strongest possible chemisorption, we see that, all other things being equal, the molecule should form two bonds rather than one.

The triangular model is to be preferred to the trapezoidal. The

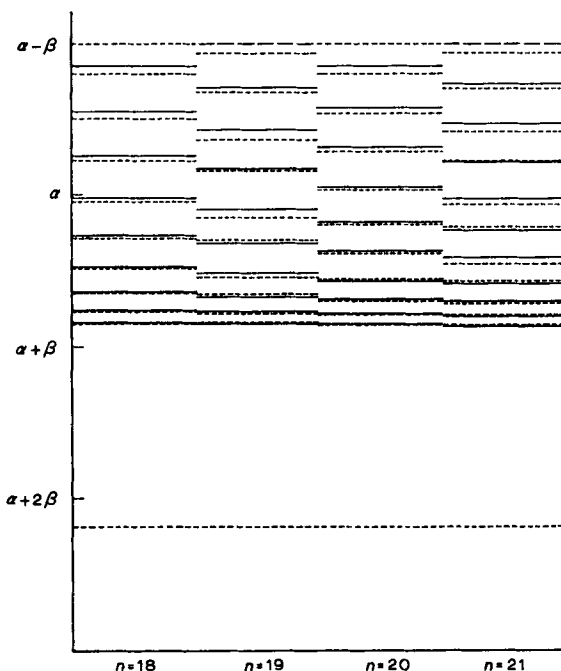


Fig. 15. Energy levels as a function of the number of long-chain atoms. Left: for the metal containing n atoms; right: for the complex containing $n + 3$ atoms. A dotted line indicates that the corresponding level is only half-filled (one electron).

semi-empirical adjustment of parameters is possible for the triangular model by means of the d orbitals and leads to the following values for all the transition metals of the first series:

- (1) in the case of chemisorption, $x = 0$, $b_1 = \frac{5}{4}$, $b_2 = \frac{1}{2}$;
- (2) for the potential barrier, $x = 1$, $b_1 = \frac{2}{3}$, $b_2 = \frac{1}{4}$.

Because of the very approximate definition of the potential barrier and above all because of the considerable approximations

involved in the use of the localized model, it is not surprising that the parameters do not agree in these two cases.

The sign of the metal is negative in agreement with experiment. A study of the triangular model gives the charges as a function of the bond integral. It shows that

- (1) chemisorbed ethylene loses some of its electrons;
- (2) for certain metals, the molecule, when it desorbs ($b \rightarrow 0$), may reverse its polarity or pick up an electron from the metal.

The change from the localized model to the deep-chain model introduces considerable corrections. These corrections can be of

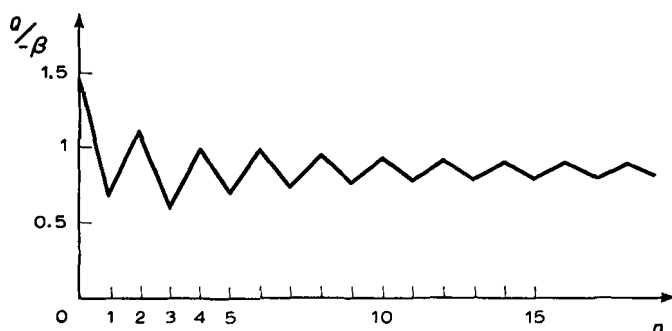


Fig. 16. Heat of chemisorption as a function of the number of atoms in the chain.

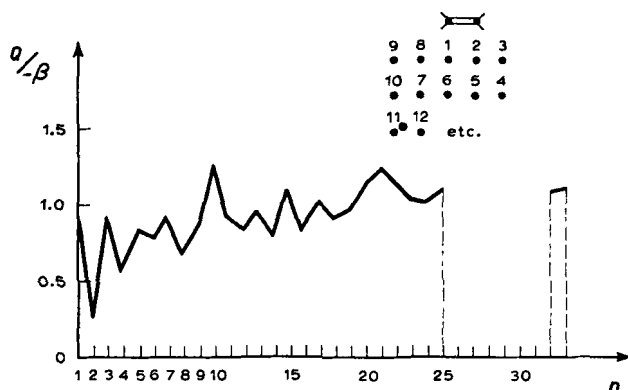


Fig. 17. Heat of chemisorption as a function of the number of electrons in the lattice.

the order of two β units but may also cancel one another. The localized model must generally be rejected; it should be used only in order to establish comparisons.

When the four parameters described in the chain are varied, it is observed that the two parameters of basic importance are b and α . The influence of s and w is very small and may scarcely be distinguished from that of b .

The extension of the chain allows us to visualize the formation of bands. Figure 15 is for metal p . The complex band is the same as that of the metal but the fine structure of the levels is different and there is now a low level. In detail, everything takes place as if this level corresponded to an orbital localized on ethylene and on the first atom. The diagram of the levels of the complex is very like that of a metal having one electron less, as if indeed the first atom were blocked off. There is, thus, the appearance of a localized bond orbital, but this does not exclude considerable energetic contributions from the metallic mass as relatively unperturbed orbitals are very numerous.

The influence of the size of the crystallites of the catalyst becomes evident below several hundred Angström units. Indeed, it is observed that the oscillations which are always present for the chain model stabilize themselves to within 1% for lengths of rows of atoms going from one hundred to several hundred (Fig. 16). There results an inequality of sites which is observable by means of a higher initial heat of chemisorption and a lower activation energy. The study of the planar lattice confirms that of the chain but the oscillations are not regular (Fig. 17).

VI. CONCLUSIONS

Such are the results obtained by the semi-empirical method using the following two hypotheses:

(1) the introduction of d orbitals in describing planar resonating systems;

(2) the treatment of a metal by the molecular method.

This second point appears to be important because, otherwise, it would be difficult to give an equally satisfactory notion of the structure of ethylene and to elaborate the notion of a site. In fact, the influence of an atom in the fourth position of the lattice

can modify the properties of chemisorption according to laws which still seem to be complex.

Such a model must be formed from an undetermined number of atoms and allows the determination of asymptotic properties. This method, which is impossible for manual calculation, is, on the other hand, very well suited to mechanical means of calculation. In this way, chain problems may be suitably resolved using analysis (ref. 83) and machines. The resulting determination of asymptotic properties is satisfactory.

On the other hand, the problem of the planar lattice seems to be at the limit of calculation by mechanical means. First of all, we tried, as we have done for the chain, to calculate the asymptotic values and their fluctuations by a process imitating that of crystallization. We believe now that it is better to separate them and to determine successively:

- (1) the best series of crystallites which allows the extrapolation of asymptotic values and gives information on the influence of the size;
 - (2) the effect of perturbations classed as functions of their distance from the ethylene molecule (the classical notion of a site has to do with its immediate neighbourhood), of their symmetry and of their nature whether superficial or deep, etc.
- The detailed discussion of the best configurations to choose to improve the study of the planar lattice brings us in fact to the general discussion of the representation of the system.

A complex problem cannot be represented in a single way no matter how detailed the representation. This is because it is not a matter of making successive approximations in the ordinary sense but rather of considering all the complexity which we would wish to introduce into the representation in one, then another, of its aspects (to be specified) always taking into account the results already obtained.

To be more specific, in the course of this research, we have passed through several stages: that of mechanisms, of localized geometric structures, that of chains with numerous electronic parameters, that of a lattice with fewer parameters, and finally that of the d orbitals in considering only a small number of localized structures.

It is simple to see what gaps remain to be filled in and what

mathematical methods can be successively used. But we wish to emphasize the two following ideas:

(1) one may specify an hypothesis only on condition that one considers other hypotheses as being at least temporarily justified;

(2) the plurality of points of view is indispensable when one considers a problem which is not known in its general lines as is the case for molecular structure or perfect crystals.

Nevertheless, the arbitrariness, both in the choice and in the development of the successive trials, remains a disturbing factor in a discipline whose essential means of study is formed by information machines. Why cannot the logic which requires one trial after another be itself a programme?

In a previous paper, one of us proposed that it was necessary to arrive at chains of iterations similar to successive approximations but concerning both the framework and the contents of the formation in question. These chains could be represented schematically in the following way:

(1) choice of a mode of representation R_1 ;

(2) the choice within this mode of representation of a reasonable approximation A_1 ;

(3) determination of a second mode of representation R_2 deduced from R_1 and taking into account A_1 , etc.

According to these ideas the representations R_1 , R_2 , etc., were *a priori* forms of wave functions the approximations A_1 , A_2 being their precise numeric definitions. One could then try to express the chain $R_1 \rightarrow A_1 \rightarrow R_2 \rightarrow A_2$ mathematically, and to render the whole process automatic.

The correspondence $R_1 \rightarrow A_1$ could result from successive approximations by the method of the error potential,⁸⁰⁻⁹⁰ which could be limited in advance either by the number of iterations or by the remaining acceptable error or by a combination of the two in order not to risk fixing the chain.

The correspondence $A_1 \rightarrow R_2$ was not explicit. The idea consisted of dividing R_1 into equivalent domains and comparing the complexity of the information obtained in each of these domains when the passage $A_1 \rightarrow R_2$ was carried out, and giving them a proportional value in R_2 .

The idea of a wave function of a fixed number of corpuscles

was used because we were thinking in terms of the molecular problem and because the wave functions gave an *a priori* framework to its representation.

In the quantum study of a complex system, the number of particles to be used to resolve the problem is by no means decided by its terms, and neither periodic nor finite models can be ignored. In addition, a more abstract schematization is necessary.

Thus, in this problem, which also presents us with difficult unknowns such as the geometric structure and the chemical mechanism, it seems unrealistic to adopt such a rigorous approach. We have, however, kept the spirit of it.

The more remarkable results obtained are therefore neither absolute certitudes not even related to a universal method of approach. These facts are probably the three following:

(1) The chemisorbed ethylene molecule is placed in profile, its centre facing a metallic atom.

(2) The size of the crystallites causes the initial heat of chemisorption to increase and the apparent potential barrier to decrease when the size is smaller than a few hundred Ångström units.

(3) While desorbing the molecule can reverse the polarity or extract an electron from the metal; the existence of these effects depends on small variations in the nature or perhaps the state of the metal.

These facts are therefore only lines of experimental research, hypotheses for the theoretical elaboration of other results, or the delimitation of areas within which more mathematical information may be obtained.

References

- 1(a) Strachan, C., Lennard-Jones, J. E., *Proc. Roy. Soc. London* **150**, 442 (1935).
- (b) Lennard-Jones, J. E., and Devonshire, A. F., *Proc. Roy. Soc. (London)* **156**, 6-9, 37 (1936).
- (c) Lennard-Jones, J. E., and Devonshire, A. F., *Proc. Roy. Soc. (London)* **158**, 242-253, 269 (1937).
- (d) Lennard-Jones, J. E., and Strachan, C., *Proc. Roy. Soc. (London)* **158**, 591 (1937).
- (e) Lennard-Jones, J. E. and Goodwin, E. T., *Proc. Roy. Soc. (London)* **163**, 101 (1937).
- (f) Lennard-Jones, J. E., *Proc. Roy. Soc. (London)* **163**, 127 (1937).
- (g) Devonshire, A. F., *Proc. Roy. Soc. (London)* **163**, 163 (1937).

2. Young, D. M., *Trans. Faraday Soc.* **47**, 1228 (1951).
3. Lenel, F. V., *Z. Phys. Chem.* **B23**, 379 (1933).
4. Barrer, R. N., *Proc. Roy. Soc. (London)* **A161**, 476 (1937)l
5. Goodwin, E. T., *Proc. Cambridge Phil. Soc.* **37**, 221 (1939).
6. Orr, W. J. C., *Trans. Faraday Soc.* **35**, 1247 (1939).
7. Crawford, V. A., and Tomkins, F. C., *Trans. Faraday Soc.* **44**, 698 (1948).
8. Rhodin, T. N., *Discussions Faraday Soc.* **5**, 215 (1949).
9. Grimley, T. B., *Proc. Phys. Soc. (London)* **73**, 323 (1959).
10. Koutecky, J., *Phys. Rev.* (1954).
11. Koutecky, J., *Phys. Rev.* **108**, 13 (1957).
12. Koutecky, J., and Tomasek, M., *Phys. Rev.* **120**, 1212 (1960).
13. Syrkin, J. A. K., *Z. Strukt. Khim.* **1**, 189 (1960).
14. Volkenstein, T., *J. Phys. Chem. Moscow* **21**, 1317 (1947).
15. Volkenstein, T., *J. Phys. Chem. Moscow* **26**, 1462 (1952).
16. Volkenstein, T., *Akad. Nauk. Ot Khim. Nauk.* **143** (1957).
17. Bontsch Brujevitch, V. L., *J. Phys. Chem. Moscow* **25**, 1033 (1951).
18. Bontsch Brujevitch, V. L., *Zh. Phys. Khim.* **27**, 662 and 960 (1953).
19. Sherman, A., and Eyring, H., *J. Am. Chem. Soc.* **54**, 2661 (1932).
20. Sherman, A., Son, C. E., and Eyring, H., *J. Chem. Phys.* **3**, 49 (1935).
21. Brenner, S., *Discussions Faraday Soc.* **8**, 79 (1950).
22. Koutecky, J., *Dokl. Akad. Nauk S.S.S.R.* **101**, 1194 (1955).
23. Koutecky, J., *Chem. Listy* **50**, 167 (1956). *Collection Czech. Chem. Commun.* **22**, 669 (1957).
24. Koutecky, J., *Chem. Listy* **50**, 689 (1956). *Collection Czech. Chem. Commun.* **22**, 683 (1957).
25. Eley, D. D., *Discussions Faraday Soc.* **8**, 34 (1950).
26. Stevenson, D. P., *J. Chem. Phys.* **23**, 203 (1955).
27. Koutecky, J., *Collection Czech. Chem. Commun.* **22**, 669 (1957).
28. Koutecky, J., *Collection Czech. Chem. Commun.* **22**, 683 (1957).
29. Koutecky, J., *Trans. Faraday Soc.* **54**, 1038 (1958).
30. Eyring, H., Colburn, C. B., and Zwolinsky, B. J., *Discussions Faraday Soc.* **8**, 39-46 (1950).
31. Thon, N., and Taylor, H. A., *J. Am. Chem. Soc.* **75**, 2747 (1953).
32. Coulson, C. A., and Longuet-Higgins, H. C., *Rev. Sci.* **85**, 929 (1947).
33. Daudel, R., and Sandorfy, C., *Bull. Soc. Chim. France* **V**, 358 (1948).
34. Sandorfy, C., *Thesis D.Sc.* (1949).
35. Grimley, T. B., *Advan. Catalysis* **12**, 1 (1960).
36. Volkenstein, T., *Advan. Catalysis* **12**, 189 (1960).
37. Lifshic, —, —, *Zh. Eksperim. i Teor. Fiz.* **29**, 94 (1955).
38. Dzialoshinskij, —, —, Lifshic, —, —, and Pitaevsky, —, —, *Inst. Probl. Phys. Acad. Sci. S.S.S.R.*
39. Krupp, H., Sandstede, G., and Schraumm, K. H., *Chem. Ing.-Tech.* **32**, 99 (1960).
40. Roche, J., *Le rôle des métaux dans la structuré et dans l'activité des enzymes*, Herman, Paris, 1946.
41. Goudot, A., *Compt. Rend.* **247**, 932 (1958).

42. Goudot, A., *Col. Phys. France* **22**, 10950 (1960).
43. Beeck, O., *Discussions Faraday Soc.* (1950).
44. Beeck, O., *Advan. Catalysis*, **2** (1950).
45. McGabe, C. L., and Halsey, G. D., *J. Am. Chem. Soc.* **74**, 2732 (1952).
46. Jenkins, G. I., and Rideal, E., *J. Chem. Soc.*, 2490 and 2496 (1955).
47. Farnsworth, H. E., and Woodcock, R. F., *Advan. Catalysis* **9**, 123 (1957).
48. Cunningham, R. E., and Gwathmey, A., *Advan. Catalysis* **9**, 25 (1957).
49. Hindin, S. G., and Weller, S. W., *Advan. Catalysis* **70** (1957). *J. Phys. Chem.* **60**, 1501 (1956).
50. Stephens, S. J., *J. Phys. Chem.* **62**, 714 (1958).
51. Foss, J. G., and Eyring, H., *J. Phys. Chem.* **62**, 103 (1958).
52. Roguinsky, S. Z., *Probl. Kinetiki i Kataliza, Akad Nauk S.S.S.R.*, **6**, 9 (1949).
53. Roguinsky, S. Z., *Probl. Kinetiki i Kataliza, Akad Nauk S.S.S.R.*, **8**, 110 (1955).
54. Roguinsky, S. Z., *Sc. chim. ind.* **2**, 138 (1957).
55. Roguinsky, S. Z., *Ed. de l'Acad. Sc. U.R.S.S.* (1949).
56. Liachenko, V. I., and Vitoutchenko, V. G., *J. Phys. Tech. U.S.S.R.* **28**, 447 (1958).
57. Pchejetsky, S. I., and Miasnikov, I. A., *Probl. Kinetiki i Kataliza, Akad Nauk S.S.S.R.* **8**, 175 (1955).
58. Pchejetsky, S. I., and Miasnikov, I. A., *Probl. Kinetiki i Kataliza, Akad Nauk S.S.S.R.* **8**, 34 (1955).
59. Liachenko, V. I., and Stepko, I. I., *Bull. Acad. Sci. U.S.S.R. Phys. Ser.* **21**, 201 (1957).
60. Terenine, A. N., *J. Chim. Phys. de l'U.R.S.S.* **6**, 189 (1935). (1955).
61. Terenine, A. N., *Probl. Kinetiki i Kataliza, Akad Nauk S.S.S.R.* **8**, 17
62. Germain, J. E., *Catalyse Hétérogène*, Dunod, Paris, 1959.
63. Germain, J. E., *Compt. Rend.* **238**, 236, 345 (1954); *J. Chim. Phys.* **51**, 263, 691 (1954).
64. Aigrain, P., and Dugas, C., *L. Elektrochem.* **56**, 363 (1952).
65. Hauffe, K., and Schlosser, E. G., *Dackema Monographien* **26**, 222 (1956).
66. Hauffe, K., *Angew. Chem.* **67**, 189 (1955).
67. Hauffe, K., *Advan. Catalysis* **7**, 212 (1955).
68. Hauffe, K., *Advan. Catalysis* **9**, 187 (1957).
69. Hauffe, K., *Bull. Soc. Chim. Belges* **67**, 417 (1958).
70. Weitz, P. B., *J. Chem. Phys.* **21**, 1531 (1953).
71. Boudart, M., *J. Am. Chem. Soc.* **74**, 1531 (1952).
72. Dowden, D. A., *J. Chem. Soc.* **242** (1950).
73. Roguinsky, S. Z., *Compt. Rend. Acad. Sci. U.R.S.S.* **67**, 97 (1949).
74. Volkenstein, T., *Zh. Fiz. Khim.* **22**, 311 (1948).
75. Volkenstein, T., *Zh. Fiz. Khim.* **23**, 917 (1949).
76. Volkenstein, T., *Zh. Fiz. Khim.* **24**, 9 (1950).
77. Wagner, C., *J. Chem. Phys.* **18**, 69 (1950).

78. Hauffe, K., Glang, —, —, and Engel, —, —, *Z. Chem.* **201**, 223 (1952).
79. Voltz, S. E., and Weller, S., *J. Am. Chem. Soc.* **75**, 5227 (1953).
80. Laforgue, A., *Cahiers Phys.* **57**; **58**, 23; **59**, 16; **63**, 18; **63**, II.
81. Daudel, R., *Structure électronique des molécules*. Gauthier-Villars, Paris, 1962.
82. Daudel, R., Moser, C., and Lefebvre, R., *Quantum Chemistry*.
83. Gouarné, R., *Thesis*, Paris (1956).
84. Sutula, V. D., and Zeif, A. P., *Kinetici i Kataliza* **3**, 698 (1962).
85. Sutula, V. D., *Kinetici i Kataliza* **3**, 704 (1962).
86. Tapilin, V. M., *Kinetici i Kataliza* **3**, 709 (1962).
87. Volkenstein, T., *Théorie électronique de la catalyse sur les semi-conducteurs*. Masson, Paris, 1961.
88. Germain, J. E., *J. Chim. Phys.*, 691 (1954).
89. Laforgue, A., Potential Error Methods. Summer school in theoretical chemistry. (August, 1959) Lidingö-Suède. (Unpublished).
90. Laforgue, A., *Cahiers Phys.* **112**, 495 (1959).

STEROIDS, PURINE-PYRIMIDINE PAIRS AND POLYCYCLIC AROMATIC CARCINOGENS*

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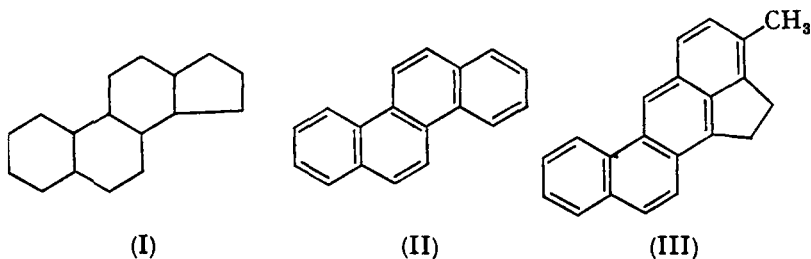
Among the recent attempts to develop the theory of chemical carcinogenesis one encounters a number of speculations on the possible role in tumor formation of different factors which may be generally termed as physical or sterical. We have recently discussed in detail on a few occasions the theories involving the physical factors, among them the electron or excitation transfer mechanisms.^{27,32,25,24} In this communication, we should like to discuss, at least in part, some of the propositions concerning the role of steric effects in carcinogenesis by polycyclic aromatic hydrocarbons.

The possible importance of size and shape for the manifestation of carcinogenic activity was suggested a long time ago by a number of authors, among whom one should mention in particular Bergmann.¹ The relation to size is, of course, inherent in the very fact that carcinogenic activity is generally restricted to aromatic hydrocarbons composed of 4, 5 or 6 fused benzene rings and is generally absent in smaller or larger molecules of this kind. This is an obvious observation which Bergmann considered as possibly meaning that the carcinogens are adsorbed by an acceptor possessing a definite adsorption area. This sets an upper limit for the dimensions of the active compounds. A lower limit is given by a decrease in adsorbability with decreasing size of the molecule. While such a concept is defensible (although in no way can it be considered as the only possible one, for factors such as solubility are also able to account for the inactivity of big molecules), it is obvious that it does not explain the observed difference in activity

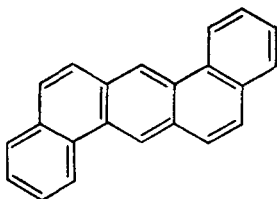
* This research was supported by grant CY-3073 of the U.S. Public Health Service (National Cancer Institute) and Convention 61-FR-134 of the Délégation Générale à la Recherche Scientifique et Technique (Comité Cancer et Leucémie).

inside the group of compounds composed of 4 to 6 fused benzene rings. For this, other factors have to be involved.

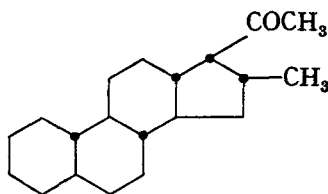
In the limits of the steric concept, such factors have recently been proposed to reside in the geometrical analogy between the steroids and the carcinogenic aromatic hydrocarbons. It has been known for a long time that the ring systems of such hydrocarbons, and in particular those of the benzanthracene-type of carcinogens, bear a strong resemblance to those of steroid hormones (at least when both are written on a planar sheet of paper). Actually, as is well known, a good deal of work has been carried out in connection with the possible *in vivo* conversion of steroids (in particular cholesterol) into a carcinogen. As is also well known these researches did not, however, yield any positive result. Nevertheless the observations on geometrical similarities between the steroids and the aromatic carcinogens have been revived recently by Yang *et al.*,³⁷ Wong *et al.*,³⁵ and Huggins¹⁴ although in a different form. Following these authors, a polynuclear aromatic hydrocarbon must bear steric resemblance to steroids in order to be carcinogenic, the possible implication of this requirement being that such hydrocarbons may act on the same sites as steroid hormones. It is not our intention to discuss here this last biodynamic aspect of the hypothesis. The point to which we wish to draw attention is the further statement of the aforementioned authors that "among polynuclear aromatic hydrocarbons of similar electronic properties, the closer the steric resemblance to a steroid, the higher the carcinogenicity".³⁶ This seems to be a disputable proposition. Thus, the essential ring skeleton of the steroids is that of perhydrocyclopentanophenanthrene (I). The aromatic hydrocarbon which resembles this skeleton most is chrysene (II), itself inactive and whose methy-



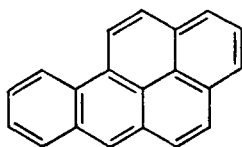
lated derivatives are only moderately carcinogenic. Methylcholanthrene (III) undoubtedly bears a striking similarity to steroids, which is emphasized by the presence of the isocyclic pentagonal ring fused to carbons 5 and 10 of the benzanthracene skeleton. It must, however, be observed¹⁶ that the position of this pentagonal ring is not essential for the carcinogenic activity; neither is the opening of this ring. What is important is the presence of methyl substituents on carbons 10 and 5 of benzanthracene. It may be added parenthetically that contrary to the statement of Yang *et al.*³⁷ the electronic factors account quite satisfactorily for this situation in the context of the *K*-region theory.²⁶ Substituents may be assumed to play a steric role similar to that of aromatic rings, but analogies based on such comparisons are highly disputable. Thus, Yang *et al.*³⁷ propose to account for the carcinogenic activity of 1,2,5,6-dibenzanthracene (IV) by its steric analogy to 16-methyl-17-acetylnorandrostande (V), and for that of 3,4-benzpyrene (VI) by its steric analogy to 1-methylnorandrostande (VII). Now, a hydrocarbon which is sterically more analogous to V than is IV seems to us to be picene (VIII), which is totally inactive. Similarly, 1,2,5,6-di-



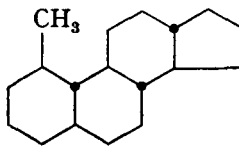
(IV)



(V)

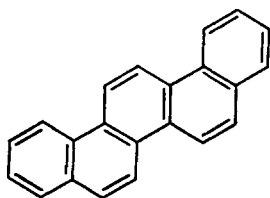


(VI)

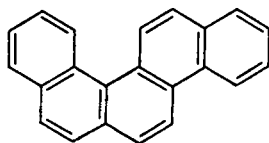


(VII)

benzphenanthrene (IX), which may be considered as being sterically as similar to VII as is VI, is nevertheless only slightly active.



(VIII)



(IX)

In fact, it may be remarked that one of the essential statements upon which Yang *et al.*³⁷ base their considerations on the significance of the geometrical analogy between steroids and carcinogenic aromatics is that "most carcinogenic polynuclear aromatic hydrocarbons contain four to five condensed aromatic nuclei." This statement which could have been considered as possibly true a number of years ago certainly does not seem any more tenable now, in particular when the carcinogenic potency is taken into account. Thus, the most carcinogenic aromatic hydrocarbons, besides 3,4-benzpyrene, are four dibenzopyrenes (the 1,2,3,4-, 3,4,6,7-, 3,4,8,9- and 3,4,9,10-isomers), composed of six fused benzene rings; and still more recently very high activity has also been observed in a hydrocarbon composed of seven fused benzene rings.¹⁷ These molecules have a greater ring skeleton than most of the active steroids.

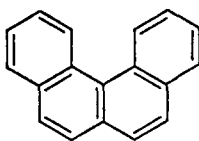
In fact, the whole concept of the steric analogy between steroids and aromatic carcinogens seems to suffer from a more fundamental drawback. The aromatic carcinogenic hydrocarbons are conjugated planar (or to a large extent so) compounds, while the steroids are essentially saturated, far from planar molecules. Although planarity is not a prerequisite for carcinogenicity¹⁵ (*vide infra*), this situation introduces important differences in the geometrical configuration of these two types of molecule. Yang seems to have partially realized the drawbacks of his proposition and in a more recent publication,¹⁴ devoted essentially to mammary carcinogens, but which obviously could just as well apply in general to active polycyclic aromatics, takes up an earlier suggestion by Haddow⁸ on the significance of the steric analogy between the carcinogenic hydrocarbons and the purine-pyrimidine complementary base pairs of the nucleic acids. He does not, however, drop the idea of the significance of the resemblance to steroids. Moreover, influenced

by certain recent publications on the subject, he considers as also important for carcinogenic activity the electron donor or acceptor properties of the molecules. He thus considers of critical significance for the determination of the carcinogenic activity of polynuclear aromatic hydrocarbons, the three following "molecular" factors:

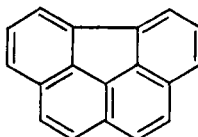
- (1) the electron transfer factor;
- (2) the geometric factor (the configuration of the hydrocarbon must resemble that of steroids *and* of the purine-pyrimidine pairs of the nucleic acids);
- (3) molecular thickness (which must not exceed the thickness of the base pairs).

It is hard to see how the authors can reconcile such different exigencies. As regards the steric factors the third condition renders meaningless the condition of resemblance to steroids. The steroids and the purine-pyrimidine pairs are too different from each other to serve simultaneously as a standard for geometrical analogies. As to the electron transfer factors, we have shown in a series of publications that they are unrelated to the presence or absence of carcinogenic activity in aromatic hydrocarbons.^{27,31,24}

In fact it is easily seen that, altogether, the three conditions are unable to distinguish between active and inactive hydrocarbons. Thus, for example, 3,4-benzphenanthrene (X) is neither a good electron donor nor a good electron acceptor; it does not par-



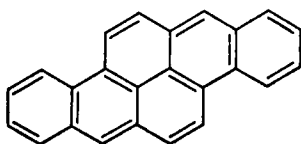
(X)



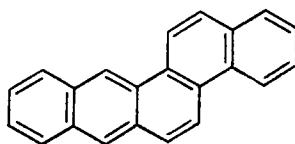
(XI)

ticularly resemble steroids and certainly not a purine-pyrimidine pair; is not even planar,¹² but nevertheless it is carcinogenic. (When the coplanarity of the four rings is enforced as in 2,13-benzofluoranthene (XI),⁶ the molecule is no more carcinogenic.)³⁶ Similarly 1,2,5,6-dibenzanthracene (IV) and picene (VIII) have similar (moderate) electron donor or acceptor properties and are of a very similar size and shape and are probably both approximately planar.⁷ Now IV is carcinogenic, while VIII is inactive.

A similar situation concerns 3,4,8,9-dibenzpyrene (XII) and 2,3,7,8-dibenzphenanthrene (XIII), the first of which is a powerful carcinogen while the second is completely inactive. Many more



(XII)



(XIII)

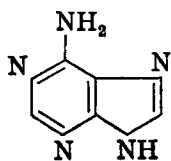
examples of this situation may be found and they all point to the conclusion that the correlations proposed by Yang *et al.* are unacceptable.

There is, however, one point in the preceding discussion which we should like to discuss further. It concerns the steric analogy between the polybenzenoid carcinogens and the purine-pyrimidine complementary pairs of the nucleic acids. It is possible that some steric analogy may be seen between these pairs and some of the aromatic carcinogens. Whatever the situation is, such an observation can hardly be translated into quantitative language and consequently can hardly form the basis for any quantitative correlation. It may, however, have some general significance, for the broader problem which has recently received much attention,^{2,3,11,22,31,24} i.e. the mechanism of the interaction between polycyclic aromatic hydrocarbons and the nucleic acids and of its significance in carcinogenesis. This question represents one of the important aspects of the recent attempts to place the whole cancer problem in the field of molecular biology to which it undoubtedly belongs, and we should like to devote now a few words to this part of the problem. (Another aspect as important, and possibly more important, is related to the interaction of carcinogens with proteins.²⁴) The fundamental observations in this field refer to the solubilization of polycyclic aromatic hydrocarbons and their substituted derivatives^{34,3} by purines, solubilization resulting sometimes in the formation of molecular complexes. More recently similar observations have been made with nucleic acids themselves.^{3,22} From the physico-chemical point of view an important indication about the nature of these inter-

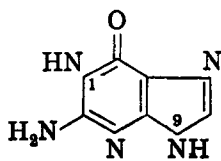
actions is the result of X-ray investigations on the molecular packing in hydroxymethyl purine crystals^{4,33} and, still more, on the molecular geometry of a 1:1 crystalline complex of 1,3,7,9-tetramethyluric acid and pyrene.⁵ These measurements established a plane-to-plane alternate stacking of the purine and pyrene molecules. As a consequence of this observation and of related crystallographic results on the mode of binding of amino-acridines with the nucleic acids,^{20,21,23} it did not seem unreasonable to suggest, as a possible mode of interaction of the aromatic hydrocarbons with the nucleic acids, the insertion of the hydrocarbons in a sandwich-like fashion between adjacent purine-pyrimidine pairs, with the resultant partial untwisting (straightening) of the helical structure in the region where the hydrocarbons are inserted. This situation raises the problem of the nature of the forces involved in such a bonding and of the significance of such a mode of interaction for the process of carcinogenesis.

Generally speaking, the forces acting in the formation of such sandwich-type complexes are referred to as *polarization* or *hydrophobic* binding, a designation which seems to include components such as van der Waals forces, dipole-induced dipole interactions, charge-transfer formation and the clustering tendency of the relatively non-polar residues of the macromolecules owing to the strong solvent-solvent interaction of water. Mutual steric fitness of the components of such a complex may, of course, play a role in such interaction, although it must be recognized that the interaction takes place readily between the purine molecules and the hydrocarbons even when the size and shape of these two types of molecules are quite different. In fact, as we shall see later, the fitness seems to be less important for the establishment of such interactions than is the intervention of steric hindrance for their prevention.

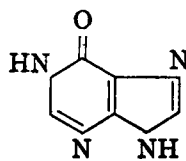
No detailed evaluation of the different factors contributing to this binding has been made yet. One quantitative relationship relevant to the binding has nevertheless been obtained. Thus we have been able to show that the *solvent power of a series of purines toward, say, a given hydrocarbon runs parallel to the electron donor properties of the purines, as measured by the value of the energy coefficient of their highest filled molecular orbital*. These values are reproduced in Table I for the essential biochemical purines and



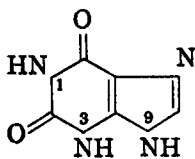
(XIV)



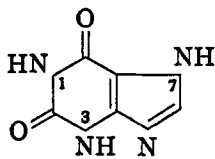
(XV)



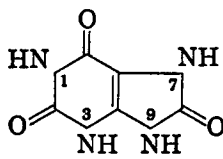
(XVI)



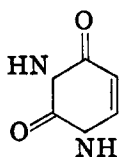
(XVII)



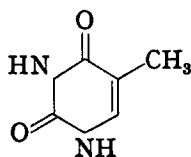
(XVIII)



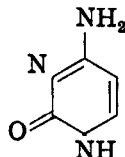
(XIX)



(XX)



(XXI)



(XXII)

pyrimidines. In agreement with our proposition it is found that the solubilizing power (e.g. toward 3,4-benzpyrene) of hypoxanthine, xanthine and adenine is small (that of hypoxanthine being, however, greater than that of adenine), while that of guanine is appreciably greater. *N*-Methylation increases the solvent power, and, moreover, the analysis of the experimental results shows that in xanthine the effect of methylation is strongest when the substitution occurs at N_3 (the next strongest effect being due to a substitution at N_7), while in uric acid it is the methylation at N_7 which has the strongest effect on the solubilizing power. For uric acid the only available data are for di- or polymethyl derivatives, but their analysis shows that the methylation increases the solvent power of the molecule in the order $N_7 > N_3 > N_9 > N_1$. Moreover, a comparison of related polymethylated xanthines and uric acids (e.g. caffeine and 1,3,7-trimethyluric acid) indicates that the methylated uric acids have a much greater solubilizing effect

TABLE I. Electron Donor Properties of Purine and Pyrimidine Bases

Compound	Energy coefficient of the highest occupied molecular orbital
Adenine (XIV)	0.486
Guanine (XV)	0.307
Hypoxanthine (XVI)	0.402
Xanthine (XVII)	0.397
Xanthine (XVIII)	0.442
Uric acid (XIX)	0.172
1-Methyl } 9-Methyl } guanine	0.303 0.302
1-Methyl } 3-Methyl } 9-Methyl } xanthine (XVII)	0.397 0.354 0.394
1-Methyl } 3-Methyl } 7-Methyl } xanthine (XVIII)	0.442 0.395 0.429
1-Methyl } 3-Methyl } 7-Methyl } 9-Methyl } uric acid	0.172 0.153 0.133 0.161
Uracil (XX)	0.597
Thymine (XXI)	0.510
Cytosine (XXII)	0.595

than the corresponding xanthines. Finally, the biochemical pyrimidines, which are poorer electron donors than the purines, scarcely show any solubilizing effect with respect to aromatic hydrocarbons.

This correlation strongly points to the conclusion that charge-transfer formation may play a role in the purine-hydrocarbon association (in the same way as it may play such a role in the stability of the nucleic acids themselves, in particular in the greater stability of the nucleic acids rich in guanine-cytosine over those rich in adenine-thymine).²⁹ It does not permit, of

course, a decision as to the relative value of this contribution to the overall association energy.

A few comments need now be made in connection with the crucial problem of the significance of this hydrocarbon-purine interaction for the process of carcinogenesis. Although such a possible complex formation has been observed, this does not mean of course that it necessarily plays a role in carcinogenesis. In fact, at least insofar as the complexes of the type observed by Boyland or the Italian scientists are concerned, there are indications against such a conclusion, e.g. methylation of the hydrocarbons which generally greatly increases their carcinogenic activity, greatly decreases their solubilization by the purines, probably because of steric interference with the sandwich-type binding, so that 9,10-dimethyl-benzanthracene and methylcholanthrene, both very potent carcinogens, are scarcely solubilized at all by the purines. A more general argument pointing in the same direction may, in fact, be given. We have shown in a number of publications²⁶ that the carcinogenic activity of the aromatic hydrocarbons seems to be intimately related to certain electronic characteristics of some specific regions of their molecular periphery (*K* and *L* regions). Now, *insofar as it is not evident* in which way such characteristics might play a role in a mechanism governing the postulated intercalation of the hydrocarbons into the nucleic acids, one is led to predict that the mere aptitude of a substance to intercalate in this way (or to form sandwich-type complexes with the purines) should not be simply directly related to its aptitude to produce cancer. This point of view seems to be confirmed, in the narrow limits of the available data, by the fact (shown both by Boyland and by Liquori *et al.*) that planar non-carcinogenic hydrocarbons (e.g. pyrene) seem to be as able, or even more able, to form complexes with purines or to interact with the nucleic acids as the related carcinogenic ones, e.g. 3,4-benzpyrene or 1,2,5,6-dibenzanthracene. (This situation may be opposed to the one concerning the interactions of the same aromatics with proteins²⁴ where the interactions: (1) seem to be related to the manifestation of carcinogenic activity, and (2) seem to involve in the carcinogens the *K* region of the molecules. This point is, however, outside the present discussion.)

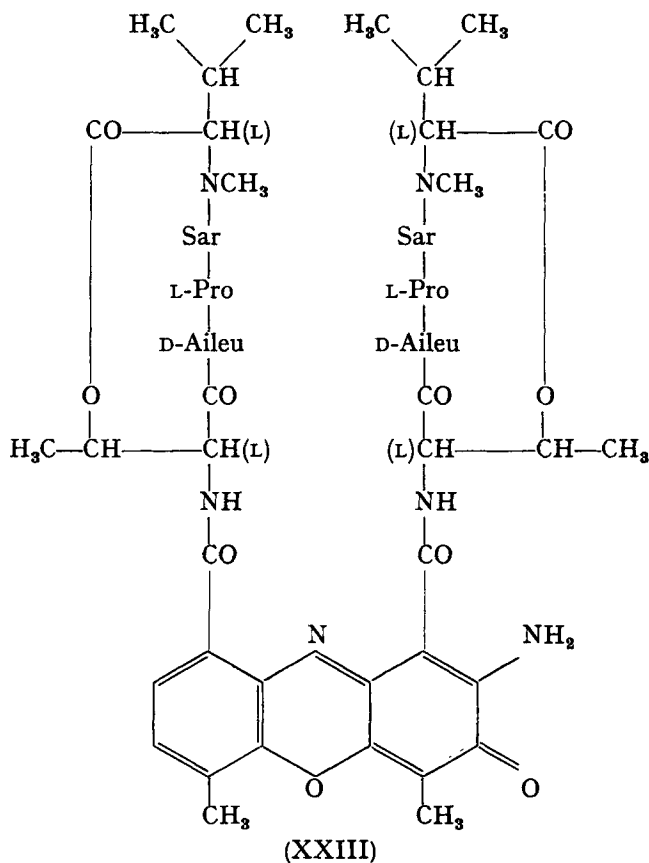
Another particular point which may be raised in connection

with this discussion is the following one. Among all the constituents of the nucleic acids, guanine is the best electron donor and this molecule may thus be expected to play a special role in the charge-transfer type of interaction. Now, although guanine is, among all the bases of the nucleic acids, the one which separately solubilizes the aromatic hydrocarbons to the greatest extent, the experimental data are insufficient to indicate any preferential interaction with guanine (or, at least, the guanine-cytosine pair) in the nucleic acids themselves. It would be most interesting to investigate the extent of the interaction of the carcinogenic hydrocarbons with the nucleic acids as a function of the guanine-cytosine content of these acids. In this field, recent observations concerning actinomycin C may perhaps be of significance. Actinomycin C (XXIII) is a highly toxic antibiotic composed of a heterocyclic ring with which are associated huge cyclic peptides. This compound forms complexes with the purines and with the nucleic acids, in particular with DNA, which from the spectroscopic view-point are similar to those formed between the aromatic hydrocarbons and the nucleic acids. It thus seems possible that the complexing of actinomycin C involves its aromatic ring, which by the way is a very good electron acceptor (energy coefficient of lowest empty molecular orbital = -0.254). It is interesting to note that in this particular case it has been possible to show that the binding of actinomycin C to DNA is probably mediated preferentially through the guanine moiety of DNA^{17,18} and that it occurs more easily with a greater guanine-cytosine content of DNA.⁸ (In fact, very recently¹⁰ the binding with guanine has been confirmed by X-ray diffraction studies. It seems to involve the phenoxazone ring of actinomycin. The postulated mode of binding seems, however, to involve essentially hydrogen bonds.)

It is time now to conclude. We have given here only a short discussion of certain aspects of some of the problems connected with the research into the factors underlying chemical carcinogenesis. These factors are certainly numerous and complex.

Size and shape may play a role but none of the propositions so far presented proves that this role is important. It must be realized that the purely qualitative way in which the steric factors are taken into account in such propositions may easily lead to very erroneous conclusions. In contrast is the much more

rigorous character of the correlations with the electronic properties and the way these have been used in a more successful way to deal with the problem.



ADDENDUM

It has been shown very recently by Heidelberger and his collaborators (Giovanella, B. C., McKinney, L. E., and Heidelberger, C., *J. Mol. Biol.* **8**, 20 (1964)) that the proposition of the English and Italian workers on the intercalation of the hydrocarbons in a sandwich-like fashion between the purine-pyrimidine pairs of the nucleic acids was, in fact, erroneous. Following the Madison

School the interaction corresponds only to the formation of a colloidal suspension of hydrocarbon particles, stabilized to some extent by DNA. This situation diminishes the significance of such an interaction for carcinogenesis. On the other hand, it does not touch upon the reality of the solubilization of hydrocarbons by free purines and upon the significance of the factors considered as being involved in this phenomenon. Generally speaking, the possibility exists that the nature of the interaction of the aromatic hydrocarbons with the nucleic acids is quite different from the nature of their interaction with the free constituents of these acids. Such a situation has been recently brought into evidence for actinomycin (Reich, E., *Science* **143**, 684 (1964); Pullman, B. *Biochim. Biophys. Acta* **88**, 140 (1964).)

For new developments and discussions see: Pullman, B., *J. Cell. Comp. Physiol.* **64**, 91 (1964) and Pullman, B., in *Molecular Biophysics*, edited by B. Pullman and M. Weissbluth, Academic Press, 1965.

References

1. Bergmann, F., *Cancer Res.* **2**, 660 (1942).
2. Boyland, E., and Green, B., *Brit. J. Cancer* **16**, 507 (1962).
3. Boyland, E., and Green, B., *Brit. J. Cancer* **16**, 347 (1962).
4. De Santis, P., Giglio, E., and Liguori, A. M., *Nature* **188**, 47 (1960).
5. De Santis, P., Giglio, E., Liguori, A. M., and Ripamonti, A., *Nature* **191**, 900 (1961).
6. Ehrlich, H. W. W., and Beevers, C. A., *Acta Cryst.* **9**, 602 (1956).
7. Ferguson, G., and Robertson, J. M., *Advan. Phys. Org. Chem.* **1**, 203 (1963).
8. Goldberg, I. H., Rabinowitz, M., and Reich, E., *Proc. Natl. Acad. Sci. U.S.* **48**, 2094 (1962).
9. Haddow, A., in *Canadian Cancer Research Conference*. Edited by R. W. Begg, Academic Press, New York, 1957, p. 361.
10. Hamilton, L. D., Fuller, W., and Reich, E., *Nature* **198**, 538 (1963).
11. Heidelberger, C., and Davenport, G. R., *Acta Unio Intern. Contra Cancrum* **17**, 55 (1961).
12. Hirshfeld, F. L., Sandler, S., and Schmidt, G. M. J., *J. Chem. Soc.*, 2108 (1963).
13. Huggins, C., in *Horizons in Biochemistry*. Albert Szent-Györgyi Dedicatory Volume. Edited by M. Kasha and B. Pullman, Academic Press, New York, 1962, p. 497.
14. Huggins, C., and Yang, N., *Science* **137**, 257 (1962).
15. Iball, J., *Nature* **201**, 917 (1964).

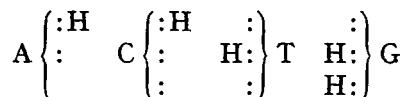
16. Inhoffen, H. H., in *Progress in Organic Chemistry*. Edited by J. W. Cook, Academic Press, New York, 1953, p. 136.
17. Kersten, W., *Biochem. Biophys. Acta* **47**, 610 (1961).
18. Kersten, W., and Kersten, H., *Hoppe-Seyler's Z. Physiol. Chem.* **327**, 234 (1962).
19. Lacassagne, A., Buu-Hoi, N. P., Zajdela, F., and Lavit-Lamy, D., *Compt. Rend.* **252**, 826 (1961).
20. Lerman, L. S., *J. Mol. Biol.* **3**, 18 (1961).
21. Lerman, L. S., *Proc. Natl. Acad. Sci. U.S.* **49**, 94 (1963).
22. Liquori, A. M., De Lerma, B., Ascoli, F., Botré, C., and Trasciatti, M., *J. Mol. Biol.* **5**, 527 (1962).
23. Luzzati, V., Masson, F., and Lerman, L. S., *J. Mol. Biol.* **3**, 634 (1961).
24. Pullman, A., *Biopolymers Symp.* **1**, 47 (1964).
25. Pullman, A., and Berthod, H., *Biochim. Biophys. Acta* **66**, 277 (1963).
26. Pullman, A., and Pullman, B., *La Cancérisation par les Substances Chimiques et la Structure Moléculaire*, Masson Editeur, Paris (1955).
27. Pullman, A., and Pullman, B., *Nature* **196**, 228 (1962).
28. Pullman, B., *Biopolymers Symp.* **1**, 141 (1964).
29. Pullman, B., and Pullman, A., *Proc. Natl. Acad. Sci. U.S.* **44**, 1197 (1958).
30. Pullman, B., and Pullman, A., *Biochim. Biophys. Acta* **36**, 346 (1959).
31. Pullman, B., and Pullman, A., *Quantum Biochemistry*, Wiley, 1963, New York.
32. Pullman, B., and Pullman, A., *Nature* **199**, 467 (1963).
33. Sutor, D. J., *Acta Cryst.* **16**, 97 (1963).
34. Weil-Malherbe, H., *Biochem. J.* **40**, 351, 363 (1946).
35. Wong, T. W., Warner, N. E., and Yang, N. C., *Cancer Res.* **22**, 1053 (1962).
36. Wynder, E. R., and Hoffman, —, —, *Cancer* **12**, 1194 (1959).
37. Yang, N. C., Castro, A. J., Lewis, M., and Wong, T. W., *Science* **13**, 386 (1961).

SOME ASPECTS OF THE BIOLOGICAL PROBLEMS OF HEREDITY, MUTATIONS, AGING, AND TUMOURS IN VIEW OF THE QUANTUM THEORY OF THE DNA MOLECULE

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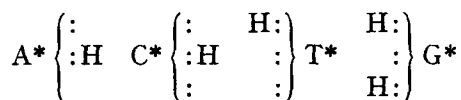
Through experimental work in the biological sciences, it is today known that the genetic information in the cell nucleus is contained in a giant molecule with the name deoxyribonucleic acid (DNA). According to the Watson-Crick model of DNA, the molecule is a double helix consisting of two sugar-phosphate chains which are held together by a large number of nucleotide base pairs. There are four nitrogen bases involved: adenine (A), guanine (G), thymine (T), and cytosine (C). The pairing is specific in the combinations A-T and G-C, and Watson and Crick have pointed out that this depends on a steric condition (a purine base always binds a pyrimidine base) and on the possibilities for formation of at least two hydrogen bonds.

Here we will focus the interest on these hydrogen bonds. In modern quantum chemistry, a hydrogen bond is simply a proton (H) shared between two electron lone-pairs (:). A study of the nitrogen bases shows that they have the following proton-electron pair code



which explains the complementarity. According to Watson and Crick, the genetic information is contained in the base sequence along one of the strands, i.e. in a four-letter sequence of the type ACGATC . . . , whereas the other strand contains the complementary sequence. Before cell division, the genetic information is duplicated by a process which involves a separation of the two strands and the formation of new complementary strands out of nucleotide material in the cellular environment.

The nitrogen bases may also occur in the rare tautomeric forms, in which a proton is moved from one lone-pair to another:



It is evident from the proton-electron pair code that these tautomeric forms have the pairing scheme A^*-C , $A-C^*$, G^*-T , $G-T^*$, which means that, at a DNA replication, the tautomeric base will combine with a wrong partner. According to Watson and Crick, this process may be responsible for the occurrence of mutations.

Here we will emphasize the fact that, since the protons are subject to the laws of quantum mechanics, there is a finite probability for the occurrence of the tautomeric forms in DNA. Each electron lone-pair attracts the proton, and this attraction may be represented by a single-well potential which is rather deep. Since the hydrogen bond contains two electron lone-pairs, the resulting potential of the proton will be a *double-well potential* with a "bump" in the middle. The minima of this potential represent classical equilibrium positions but, since the proton has the nature of a wave packet, it may penetrate the classically forbidden region and pass the potential barrier through the "tunnel effect". In spontaneous phenomena, the two bases in a pair are usually equally charged, and if a proton goes from one set to the other, the second proton goes usually the reverse way to keep the gross electrical neutrality. This means that through proton tunnelling the normal base pair $A-T$ will be changed into the tautomeric base pair A^*-T^* and similarly $G-C$ will be changed into G^*-C^* . The replication scheme is then entirely changed (cf. Fig. 1).



Fig. 1. Comparison between normal and tautomeric replication of DNA.

The proton exchange is regulated by the time-dependent Schrödinger equation, which tells us the distribution of the wave packet and the associated probability for finding the proton. At the time of a DNA replication, the proton has to "choose sides", and this leads to a new initial condition with the proton fully on one side.

The proton exchange contains a mechanism leading to the occurrence of spontaneous *mutations*. Through the proton tunnelling, there is apparently a steady loss of genetic information with time, and the question is whether this would be the primary cause of the biological phenomenon of *aging*. If the changed code has a biological meaning, there may be a somatic mutation which may lead to the development of "an individual within the individual", i.e. a tumour, and the question is whether part of the origin of cancer may be traced back to the proton tunnelling in DNA. If finally the bases within a pair are unequally charged, it is very likely that both protons in the code may turn up on the same side, and the genetic code is then irreversibly lost. This process may be of importance in connection with induced phenomena caused by radiation, mutagens, carcinogens, etc., since ionization processes and donor-acceptor reactions may lead to situations where charges are removed or added to one of the base pairs. For further details, we will refer to some other publications.¹

References

1. Lowdin, P. O., Technical Note No. 85, Uppsala Quantum Chemistry Group 1962; *Proc. Bombay Symp., Molecular Structure and Spectroscopy*, September 1962; *Rev. Mod. Phys.* **35**, (1963); *Proc. Stanford Symp., Quantum Aspects of Polypeptides and Polynucleotides* (1963); *Biopolymers Symp.* 1, 161 (1964).

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